University of Alberta

HYDROLOGICAL AND HYDROCHEMICAL INVESTIGATIONS IN A GLACIAL LAKE CATCHMENT: IMPLICATIONS FOR ORGANOCHLORINE TRANSPORT

by

MELISSA J. LAFRENIÈRE

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Dr. Mark W. Williams

Date: 15 September 2003

This thesis is dedicated to Serge, my mother
and my father who is dearly missed

"It is not possible to add pesticides to water anywhere without threatening water everywhere"

Rachel Carson, Silent Spring (1962)

Abstract

Previous observations have indicated that fish from glacially fed alpine lakes contain elevated levels of organochlorine (OC) contaminants. Trout from Bow Lake, Banff National Park, Alberta, had the highest contaminant concentrations of all the lakes surveyed in western Canada (Donald et al., 1993). Subsequent investigations showed that the elevated levels of contaminants in fish from Bow Lake could not be explained by biomagnification (Campbell et al., 2000), as has been found in similar studies of lakes at lower elevations (Kidd et al., 1995). It was determined that glacial runoff was the dominant source of OC inputs to Bow Lake, and that most OCs from this source were in the dissolved phase and hence were highly bioavailable (Blais et al., 2001a; Braekevelt, 2001). This study was conducted to determine why glacial runoff is a major source of OC contaminants. The research focuses on the roles of water sources and flow routing in adjacent glacial and non-glacial watersheds in controlling the delivery of OCs to the lake. The conclusions are based on a combination of hydrological and hydrochemical analyses of runoff.

A combination of low forest and soil cover in the glacial catchment, and lower DOC concentrations in runoff likely contribute to high deposition, efficient delivery, and high bioavailability of OCs in glacial runoff. The presence of forests appears to reduce the total accumulation of OCs (and snow) relative to barren/sparsely vegetated areas. Thus, the lack of/limited forest cover in glacial catchments may contribute to higher OC deposition in glacial catchments relative to environments with more forest cover. DOC and solute chemistry indicate that there is likely lower retention of OC contaminants in glacial catchments due to the limited presence of organic soils and vegetation, and the

limited contact between glacial runoff and these sources of organic carbon. The lower DOC concentrations and less aromatic nature of DOC in glacial runoff could enhance the bioavailability of OC contaminants relative to snowmelt fed catchments where the flushing of soils during snowmelt provides higher concentrations of more aromatic DOC. High contributions of OCs from glacial runoff in years with extensive melt may result from multi-year storage of OCs in firn or glacier ice and/or from flushing of OCs stored within the firn aquifer during low ablation years.

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Fieldwork for this thesis was carried out over four summer field seasons (and many short winter trips) at Bow Lake between 1997-2000. Thanks to Shauna, Chris, and Katie for their assistance in summers. Thanks to Andrew Wilkinson and Jason Young for their help in the field and introducing me to OC extractions. I also owe many thanks to Jules Blais for his help in the field and Linda Kimpe for her time and effort in explaining the complexities of OC chemistry and analysis to me. Brad Thomas, deserves special mention for his hard work in the field and for putting up with me the longest (4 months!). Brad, your determination that summer was inspirational. I can't imagine anyone else who would/could carry a zodiac up a mountain. Also, I'd be willing to bet no one has ever managed to get the sauna as hot as you did! In addition I have to express my gratitude to Tony Chatham for making Mosquito a comfortable place to live and work. Thanks for providing the occasional escape from the commotion by sharing your limited space, your food, and your Santa Rita!

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List of Acronyms, Symbols, and Abbreviations

ARIMA	auto regressive integrated moving average
ANOVA	analysis of variance
BR	Bow River inflow
BG	Bow Glacier tributary
BH	Bow Hut tributary
COI	cone of influence
CV	coefficient of variation (SD/mean*100)
ENSO	El Niño southern oscillation
F	solute flux (Mass Time^{-1})
F_s	specific solute flux (Mass Time^{-1} Area^{-1})
FI	fluorescence index: ratio of emission intensity at 450:500 nm, excitation 370 nm
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DI	deionized water
DIN	dissolved inorganic nitrogen
DOC	dissolved organic carbon
GL	Glacial stream
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
MDL	method detection limit
NAO	North Atlantic oscillation
NPOC	non-purgeable organic carbon
NT	Numtijah Lodge well
OCs	organochlorines
OF	Bow Lake outflow
PCBs	polychlorinated biphenyls
PDO	Pacific decadal oscillation
POC	particulate organic carbon
Q	discharge/runoff (Volume Time^{-1})
Q_s	specific discharge/runoff (Volume Time^{-1} Area^{-1})
SD	standard deviation
SE	standard error
SOI	southern oscillation index
SWE	snow water equivalent
T	air temperature (degrees Celcius)
TFN	Transfer Function-Noise

α	lag-1 autocorrelation coefficient
λF_{max}	wavelength of peak fluorescence
$\psi(t)$	the wavelet function
$\theta_n^{XY}(s)$	phase difference
$W_n(s)$	the wavelet transform
$W_n^{XX}(s)$	wavelet power spectrum
$W_n^{XY}(s)$	cross-wavelet spectrum (bi-variate)
$\overline{W}_n^{XX}(s)$	global (time averaged) wavelet spectrum

Chapter 1. Introduction

1.1 BACKGROUND

1.1.1 Organochlorine Contaminants

Organochlorine (OC) contaminants are ubiquitous in the environment, including remote regions where the compounds have never been used (Galassi et al., 1997; George and Frear, 1966; Muir et al., 1995). These manufactured chemicals are neutral organic molecules comprised almost exclusively of carbon (C), hydrogen (H), and chlorine (Cl) atoms. OCs have many adverse effects on animal and human health, which have led to the restriction or prohibition of their use in most developed countries (de March et al., 1998; Hassall, 1982). Some common toxic effects include interference with normal reproduction and development, the disruption of nervous and immune systems, and the promotion of tumour growth (de March et al., 1998).

OCs include a wide range of contaminants, which differ in molecular structures and uses. The contaminants considered in this thesis fall into two classes: organochlorine pesticides and polychlorinated biphenyls (PCBs). PCBs were introduced in 1929 and have been widely used as insulating fluids in transformers and capacitors, heat transfer fluids, and hydraulic fluids, and although their use is currently banned in most developed countries, large amounts still exist in large transformers and capacitors (de March et al., 1998). There are 209 PCB congeners (i.e. isomers and compounds exhibiting different numbers of chlorine atoms). The number of chlorine atoms and their distribution influences the physical and toxicological characteristics of the PCBs (Schwarzenbach et al., 1993). Organochlorine pesticides are usually divided into four main groups (de March et al., 1998; Hassall, 1982): DDT (dichlorodiphenyltrichloroethane) and its analogues, the HCHs (hexachlorocyclohexanes), the chlorinated cyclodienes (e.g. aldrin, dieldrin, chlordanes), and polychlorobornanes and camphenes (e.g. Toxaphene). The use of most OC pesticides (e.g. DDT, dieldrin, chlordanes, Toxaphene) was banned or restricted in most developed countries sometime between the late 1970s and late 1980s. Lindane (the γ-HCH isomer) is one of the only OC pesticides that is currently used in North America and Europe. Most other OC pesticides have been replaced with other less persistent nitrogen and phosphorus based pesticides, or with OCs with oxygen and sulphur (e.g. endosulphan) substitutions (de March et al., 1998).

Despite their structural differences all of these compounds share characteristics that promote their widespread distribution and accumulation in the environment: they are persistent, hydrophobic, lipid soluble, and semi-volatile[1]. The relatively high vapour pressures[2] of most organochlorines lead to their volatilization and subsequent long-range atmospheric transport. Their persistence is a result of the chemical stability of the C-C, C-H and C-Cl bonds (Hassall, 1982). This chemical stability combined with the low aqueous solubility[3] and the highly lipophilic nature of neutral organic molecules leads to their accumulation and biomagnification in the environment (Hassall, 1982). The term OC is used throughout the thesis to refer to both OC pesticides and PCBs.

1.1.2 OCs in cold environments

OC compounds tend to evaporate from warm source regions, and are transported long distances in gas and particulate phases in the atmosphere before they are deposited (Barrie et al., 1992). The concentration and deposition of semi-volatile OCs increase with increasing latitude and/or altitude, and increasing volatility of the compound. This effect is attributed to 'cold condensation' and 'global fractionation' processes (Blais et al., 1998; Wania and Mackay, 1993).

Global fractionation and cold condensation were proposed as explanations for the spatial distribution and deposition of OC contaminants in the Arctic environment (Wania and Mackay, 1993). Cold condensation refers to an increase in the tendency for OCs in the atmosphere to condense from the vapour phase onto particles (e.g. water, aerosols, snow, ice) with decreasing temperatures. The increase in the proportion of contaminants in condensed phases enhances the removal of OCs from the atmosphere because OCs associated with aerosol particles tend to be deposited more rapidly than contaminants in the vapour phase (Franz et al., 1997; Wania and Mackay, 1993). Global fractionation refers to the latitudinal separation of OCs due to differences in the vapour pressures of contaminants (Wania and Mackay, 1993). OCs with higher vapour pressures (i.e. more volatile compounds) will reach their condensation point at lower ambient temperatures. More volatile compounds will therefore be likely to travel further (to colder regions) before condensing and being deposited. The enhanced deposition of more volatile organochlorines with altitude is attributed to an analogous 'altitudinal' fractionation (Blais et al., 1998).

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[1] Semi-volatile compounds are those that, under normal temperatures and pressures, can have a substantial fraction of their mass in the vapour phase (Barrie et al., 1992).

[2] The vapour pressure is the pressure of the vapour of a compound at equilibrium with its pure condensed phase (Schwarzenbach *et al.*, 1993 p. 56)

[3] Aqueous solubility is defined as the abundance of a chemical per unit volume in the aqueous phase when the solution is in equilibrium with the pure compound at a specified temperature and pressure (Schwarzenbach *et al.*, 1993 p. 76)

1.2 CONTEXT AND RATIONALE

This thesis is part of an interdisciplinary study investigating the reasons for the high concentrations of OCs in the fish at Bow Lake, Alberta (Blais et al., 2001a, 2001b; Braekevelt, 2001; Campbell, 1997). The impetus for this project was evidence of elevated levels of OC contaminants in fish of some high altitude lakes in the Canadian Rocky Mountains (Donald et al., 1993). Both the atmospheric deposition of OCs (Blais et al., 1998) and the concentrations of certain OCs in fish (Donald et al., 1993) increase dramatically with elevation. Among the lakes surveyed in western Canada, glacially fed lakes (e.g. Bow Lake) yielded lake trout containing higher OC concentrations than snowmelt fed lakes. For several contaminants, trout from Bow Lake had the highest concentrations of all the lakes surveyed in western Canada (Donald et al., 1993, 1998). Subsequent investigations showed that the elevated levels of contaminants in the fish at Bow Lake could not be explained by biomagnification along the food chain (Campbell et al., 2000), as was found in similar studies of lakes at lower elevations (Kidd et al., 1995; Rasmussen and Rowan, 1990). These results suggested that the elevated levels of contaminants in the aquatic ecosystem might be due to processes or physical characteristics unique to glacial environments.

Glacial catchments differ substantially from non-glacial catchments in terms of water sources, hydrological flow routing, and sediment and soil characteristics in ways that are likely to enhance OC deposition, and limit volatilization and catchment retention relative to non-glacial alpine environments (Barrie et al., 1992; Schindler et al., 1995). The factors investigated in the interdisciplinary study include: the importance of runoff as a source of OCs to Bow Lake (Blais et al., 2001a, 2001b); and the impact of suspended glacial sediments on the sorption and biological uptake of OCs (Braekevelt, 2001).

Braekevelt (2001) found that the sorption of OCs to glacial clays was very low, due to the low organic carbon content of glacial sediments (OC 1.3±0.1%). Laboratory experiments and field studies also showed that direct uptake of OCs from water (i.e. bioconcentration), rather than ingestion of particle bound OCs, is the dominant uptake route of OCs by zooplankton in Bow Lake (*Hesperodiaptomus arcticus*). Furthermore, experiments indicated that the presence of 1.5 ppm DOC resulted in a reduction of bioconcentration due to the sorption of OCs to DOC

(Braekevelt, 2001). This finding indicates that the presence of DOC, even at low concentrations, in stream and lake water is likely an important control on the bioavailability of OCs in these ecosystems.

Analysis of OC concentrations in runoff from various streams in the Bow Lake catchment showed that glacial runoff was the dominant source of OC inputs to Bow Lake, and that the OCs were largely in dissolved form (Blais et al., 2001a). Since only freely dissolved OCs can be bioconcentrated (Black and McCarthy, 1988; Larsson et al., 1992), these results indicate that the high proportion of dissolved contaminants in glacial runoff may be an important factor in the elevated levels of OCs in lake biota (Braekevelt, 2001). A study of the mass balance of OCs in the Bow Lake catchment (including fluxes from rainfall, snowfall, runoff, gas absorption, volatilization, and sedimentation) also indicated that runoff from the glacial catchment was the dominant source of many OCs to the lake (Blais et al., 2001b). Most OCs, in both snowmelt- and glacially-fed streams peaked in concentration during snowmelt, although concentrations in the snowmelt fed streams were usually much lower than in a glacially-fed stream (Blais et al., 2001a; Blais et al., 2001b). The concentrations of most OCs in the glacial stream also exhibited relatively high concentrations throughout the mid to late summer period (Blais et al., 2001b).

The results from these studies show that snowmelt runoff, especially from glacial catchments, is the principal source of OCs to Bow Lake and that glacial ice melt may also be contributing contaminants that were deposited in the past. Furthermore, the high proportion of OCs in the freely dissolved phase in the glacial stream, and the direct uptake of OCs (bioconcentration) by zooplankton suggest that the phase distribution of OCs (i.e freely dissolved vs. DOC or particle bound) in glacial runoff is an important factor in the bioconcentration of contaminants in aquatic organisms.

1.3 THESIS OBJECTIVES

The aim of this thesis is to investigate differences in water sources and hydrological flow routing of runoff between glacial and non-glacial watersheds, and determine how these differences affect the transport of organochlorine contaminants to Bow Lake. Bow Lake receives runoff from well-defined glacial and non-glacial (snowmelt) catchments, which makes the site well suited for this study. Inter and intra-annual variations in the flow routing and sources of water in the two principal streams (one glacial, one snowmelt-fed) entering Bow Lake are investigated using a combination of physical (hydrological and meteorological) and chemical (dissolved inorganic and organic solute content, and isotopic composition) parameters. Data collection and fieldwork spanned four consecutive years (1997-2000). This period included a strong ENSO (El Niño Southern Oscillation) cycle, so the data set provides a unique opportunity to examine the hydrological regimes of the glacial and non-glacial streams, and their influence on stream OC budgets under contrasting hydroclimatological conditions.

The relative contribution of the different water sources (rain, snow, ice, and groundwater) to runoff should influence the amount of OCs transported from a catchment because different water sources may have different initial OC loadings. For example, because snow is formed at colder temperatures it will likely have higher concentrations of contaminants than rainwater, due to the cold condensation effect (Wania and Mackay, 1993). Snow is also much more effective at scavenging atmospheric contaminants than rain because of its high porosity and surface area (Franz and Eisenreich, 1998). The OC load in ice will vary depending on its age. Ice that was formed prior to 1945 should be free of contaminants, while ice formed since then will contain relatively high contaminant concentrations. The concentrations of many OC contaminants in ice formed between 1970-1990 were equal to or higher than the concentrations found in contemporary snow (Blais et al., 1998; Donald et al., 1999).

Flow routing could influence the degree of revolatilization and retention of OCs in a catchment because the nature of the hydrologic pathway determines the contact times between water and the atmosphere, soils, and sediments. Meltwater on the surface of a glacier percolates downward through snow and firn to form a saturated layer on the surface of the ice, and then flows into the glacier via crevasses. Where ice is exposed, runoff flows directly over the ice surface to crevasses or ice margins (Fountain and Walder, 1998). After entering a crevasse, meltwater flow in a temperate glacier is channelised in ice walled conduits before reaching the glacier bed, and the bulk of it remains channelised as it passes through glacier and into proglacial area. Water flow through temperate glaciers therefore effectively isolates meltwater from the atmosphere and limits the potential for loss of contaminants from meltwater by volatilization. Also, since very little runoff is involved in flow through saturated subglacial sediments (Fountain and Walder, 1998), glacial flow routing limits meltwater contact with sediments and organic matter and may restrict the retention of OCs within glacial catchments. In non-glacial catchments snowmelt will generally occur as either overland or near-surface flow in the upper soil horizons (Boyer et al., 1997). Both the contact time with and the abundance of organic soils or sediments will likely be greater than in glacial environments, or recently deglaciated terrain. Where snow overlies vegetation or soils, much of the contaminants in the snow will likely be immobilized by sorption to organic matter during snowmelt. Therefore, seasonal changes in water sources and flow routing in glacial and non-glacial catchments may result in differential volatilization and retention of OCs.

One of the goals of the Bow Lake project was to determine the physical factors underlying the high concentrations of OCs in the food webs of high altitude lakes in order to develop predictive models of contaminant deposition and accumulation in high altitude lakes. This thesis should contribute to this end by determining the effects of catchment features (such as soil, vegetation cover, and glacial cover), hydrological processes (such as the flow routing of runoff through glacial environments and soils), and short-term climate variability (e.g over an ENSO cycle) on the deposition and runoff of organochlorines in a glacial lake catchment.

1.4 THESIS OUTLINE

The thesis is presented as a series of four papers (outlined below), with a final chapter that draws together the main conclusions and discusses the implications for OC transport. Each of the four papers (Chapters 2-5) was written as an individual manuscript. The first three use stream discharge and meteorological records, as well as the concentration and characteristics of dissolved organic carbon (DOC) and dissolved inorganic solutes to identify and compare inter and intra- annual variability in the major water sources and hydrological flow routing in the two catchment types. These papers were written without reference to the results of OC analysis, however the implications of these results for the transport of OCs are discussed in Chapter 6. Chapter 5 examines the OC concentrations in snow, snowmelt, and streams in 1997 and 1998. The specific objectives of the four papers are as follows:

Paper 1: To investigate and compare the runoff regimes of the principal glacial and non-glacial tributaries to Bow Lake and their inter-annual variability over an El Niño Southern Oscillation (ENSO) cycle

Wavelet analyses of air temperature, discharge and rainfall records are used to interpret and compare the seasonal and inter-annual variability of hydrological processes operating in the two catchments over four consecutive summers (1997-2000). The relationship between stream discharge and air temperature (a proxy for solar melt energy input) evolves as the melt season progresses due to changes in snowpack extent, the exposure of glacial ice, and the storage of melt water in the snowpack, glacier (i.e. due to development of englacial and subglacial drainage systems), and/or shallow soils and groundwater. Therefore, differences in the relationship between temperature and discharge reflect changes in the dominant runoff sources (snow, glacier ice, and rainfall), and in catchment flow routing. As the period of investigation includes the strong 1998 El Niño event, the data illustrate the influence of short-term variations in hydroclimatological conditions on the hydrological regimes of the glacial and non-glacial streams.

Paper 2: To investigate differences in the degree of contact between runoff and organic matter in glacial and non-glacial environments.

Organic matter in almost any form is a more favourable solvent, or sorbent, for OCs than water (Braekevelt, 2001; Chiou et al., 1983, 1986; Schwarzenbach et al., 1993). Therefore, the fate of OCs dissolved in snow and ice melt, will be significantly affected if there is opportunity for solid-aqueous, or solvent (e.g. DOC)-water exchange reactions. Spectrofluorometric techniques permit the differentiation of DOC that is derived primarily from a terrestrial source (from soil or plant organic matter) from DOC of microbial origin (from by-products and leachate of algae and bacteria, McKnight et al., 2001). Thus, the spectrofluorometric character of DOC can help determine the likely source of DOC and the flow routing of runoff. The variability in the fluorescent properties of DOC is largely due to differences in the aromatic carbon content of terrestrial and microbially derived humic substances (Chin et al., 1994; McKnight et al., 2001). DOC derived from terrestrial sources contains fulvic acids from plant litter and soil organic matter, which are generally more aromatic than humic materials formed from extracellular and/or decomposition by-products of microbial activity (McKnight et al., 1994; Thurman, 1985; Wagner and Wolf, 1999). The chemical properties of the DOC may therefore be an important factor in contaminant-DOC interactions, since the binding of OC contaminants to DOC is enhanced by higher concentrations and aromaticity (or lower polarity) of DOC (Carter and Suffet, 1982; Chiou et al., 1986). Thus, the bioavailability of OCs may depend upon both the quantity and quality of the DOC in runoff.

This paper examines the concentration and spectrofluorometric properties of DOC in the surface waters (snow melt, soil, and stream waters) of adjacent glacial and non-glacial catchments. It then investigates differences in the provenance and abundance of DOC in runoff, and their implications for hydrological flow routing, and contact with organic environments in the two catchments.

Paper 3: To determine how the inorganic solute chemistry of runoff responds to seasonal and inter-annual changes in flow routing and runoff volume, and to differences in physical catchment properties (e.g. vegetation cover, ice cover).

This paper investigates the flux of solutes in the two catchments under different climatic conditions, to determine how solute chemistry changes with changes in the dominant sources of runoff (snow, glacier ice, and rainfall) and flow routing inferred from the previous studies. Changes in annual snow depth and melt rates can affect flow routing (Hardy et al., 2001), and the extent to which the chemical composition of runoff is influenced by biogeochemical processes in soils (Brooks et al., 1995; Fitzhugh et al., 2001). In a glacial catchment, snow and ice melt should dilute the baseflow solute concentrations, and inter-annual variations in meltwater flux and the degree of subglacial drainage system development should affect solute generation as a result of changes in flow routing and water:rock contact times. These variations may alter the balance of weathering reactions that yield solute to glacial meltwaters by controlling the extent to which waters have access to chemically reactive rock flour, atmospheric carbon dioxide (Brown et al., 1994), and environments in which microbially mediated reactions take place (Tranter et al., 1994; Tranter et al., 2002). These hydrochemical changes will affect processes such as nutrient and carbon budgets (Boyer et al., 1997; Brooks et al., 1995), and the transport of organic contaminants (Blais et al., 2001a; Blais et al., 2001b).

Paper 4: To examine local and inter-annual variability in OC deposition to the snowpack, and the transfer of OCs from snow to snowmelt and stream runoff in the glacial and non-glacial catchments.

The principal source of contaminants to alpine catchments is snow, so the contaminant burden delivered to the aquatic ecosystem in high altitude lakes will largely depend on the amount of contaminant deposited to the snowpack and the efficiency of the transfer of the snowpack OC burden to meltwater and streams. The aim of this study is to better understand the transfer of OCs from the snowpack to the tributaries in the Bow Lake catchment. Analyses of snow, snowmelt and stream OC samples collected at Bow Lake are presented for two contrasting hydrological years (1997 and 1998). The controls on the spatial and inter-annual variability in the abundance and composition of OCs in the snowpack are examined. The concentration and/or fractionation of OCs during snowmelt are investigated using measurements of OC concentrations in meltwater collected in snowmelt lysimeters from two different sites. Then the relationship between OC concentrations in samples from one glacial and one non-glacial stream and winter snowpack concentrations, water sources and hydrological pathways are examined. Much of Canada receives a significant proportion of its total annual precipitation as snow, and derives a large part of its surface waters from mountainous regions that accumulate organic contaminants (Blais et al., 1998; Donald et al., 1999). Yet, most of the work on the composition and behaviour of organic contaminants in snow and snowmelt has been carried out in the Canadian Arctic (Gregor, 1990; Gregor and Gummer, 1989; Gregor et al., 1995; Hargrave et al., 1988). This study is the first to examine local and inter-annual variability in OC deposition to the snowpack, and the transfer of OCs from snow to snowmelt and stream runoff in a headwater catchment of a major drainage basin of Western Canada.

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Chapter 2. Wavelet analysis of inter-annual variability in the runoff regimes of glacial and non-glacial stream catchments, Bow Lake, Alberta[1]

2.1 INTRODUCTION

Runoff from alpine catchments is typically dominated by snow and ice melt, which peak in spring and summer. Intra- and inter-annual variability in runoff regimes results from variations in winter snowfall and summer meteorological conditions. In some areas, variability at both time scales may be strongly coupled to atmospheric teleconnection patterns such as the El Niño Southern Oscillation (ENSO), the Pacific Decadal Oscillation (PDO), and the North Atlantic Oscillation (NAO) (Brown, 1998; Dracup and Kahya, 1994; Kahya and Dracup, 1993; Moore and Demuth, 2001; Redmond and Koch, 1991). Inter-catchment differences in runoff regimes may reflect differences in the dominant runoff sources (snow, glacier ice, and rainfall) and in the flow routing within the catchments. These influences also affect processes such as acidification (Stoddard, 1995), nutrient and carbon budgets (Boyer et al., 1997; Brooks et al., 1995), and the transport of organic (Blais et al., 2001a, b) and inorganic contaminants.

This paper investigates the runoff regimes of two adjacent alpine catchments (one largely glacier covered and one virtually ice-free), their relationship to meteorological forcing, and their inter-annual variability over an ENSO cycle. Wavelet analyses of temperature, discharge and rainfall time series are used to compare the seasonal and inter-annual variability of hydrological processes operating in the two catchments in four consecutive summers (1997-2000). As this period includes the strong 1998 El Niño event, the meteorological and discharge time series data provide a unique opportunity to examine the hydrological regimes of the glacial and non-glacial streams under contrasting hydroclimatological conditions.

In snow and ice covered catchments, solar radiation is the primary force driving the seasonal hydrological cycle. Although net radiation is the main energy source for melt, air temperature is usually better correlated with melt production and run-off than net radiation (Braithwaite, 1981). Therefore, air temperature is used here as a proxy for melt energy input to the catchments. As the melt season progresses, the relationship between discharge and air temperature evolves. This is due to changes in snowpack extent, the exposure of glacial ice, and the storage of melt water in the snowpack, glacier (i.e. due to development of englacial and subglacial drainage systems), and/or shallow soils and groundwater. Thus, the relationship between temperature and runoff contains information about the transfer and storage processes operating in the catchment.

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Many recent studies have applied a combination of time domain statistical techniques to climatic and hydrological time series data from glacial catchments to infer changes in the functioning of glacier drainage systems during the ablation season (Gurnell et al., 1992; Hodgkins, 2001). These techniques include linear regression, cross-correlation, ARIMA (Auto Regressive Integrated Moving Average) and TFN (Transfer Function-Noise) models. Other studies have used spectral (Fourier Transform) analysis to investigate the relationships between meteorological conditions and runoff in glacial catchments (Gudmundsson, 1970; Gudmundsson and Sigbjarnarson, 1972). This paper presents the first application of the continuous wavelet transform to the analysis of air temperature-runoff relationships. Wavelet analysis is a time dependent spectral analysis that decomposes a data series in time-frequency space. Wavelet methods have been used for more than a decade in many different types of signal and image analysis (Kadambe and Boudreaux-Bartels, 1992; Kronland-Martinet et al., 1987; Schiff, 1992). Recently, the use of wavelets has expanded into the physical earth sciences (Labat et al., 2000; Smith et al., 1998; Torrence and Compo, 1998; Whitfield and Dohan, 1997).

The lack of a static 24 h discharge cycle, and the dynamic nature of the temperature-runoff relationship make continuous quantitative analysis of the amplitude and the timing of runoff response to air temperature inputs difficult using standard time series techniques. For example, regression and cross-correlation techniques require several steps of data preparation, and the subdivision of the time series into periods of similar behaviour to evaluate seasonal changes in the time series (Gurnell et al., 1992; Hodgkins, 2001). Wavelet methods are better suited to this type of problem, because one can quantify the variability of a series continuously in time and at different scales of response. The covariance (or coherence) and the phase (or lag) relationships of paired time-series can also be quantified continuously across both scale and time, by combining the wavelet transforms of the two data sets. The introduction of statistical significance tests by Torrence and Compo (1998) has greatly improved the quantitative nature of wavelet analysis. In this paper, wavelet spectra are determined for air temperature and discharge of the two streams for four consecutive summer seasons (June-September) 1997-2000. The cross-wavelet spectra between air temperature and the two stream runoff series for each year are also determined. Wavelet spectra of rainfall and rain-runoff cross-spectra are calculated for 1999 and 2000.

2.2 FIELD SITE AND DATA

Stream discharge and meteorological data were collected at Bow Lake, Banff National Park, Alberta, Canada (51°40N, 116°27W) between June 1997 and September 2000. Two main catchments feed Bow Lake; one is largely glacier covered, the other is virtually ice-free (<1.5% glacier ice) (Figure 2.1). The principal inflow to the lake is the "Glacial" stream (GL) fed primarily by meltwater from the Wapta Icefield. The catchment of this stream is approximately 27 km^2, has a mean elevation of 2560 m.a.s.l., and consists of glacier ice (41%, 11 km^2), till, moraines, and some spruce-fir forest (12%). The secondary inflow is the headwaters of the Bow River (BR). This stream drains into the north side of Bow Lake, and its catchment has a mean elevation of 2310 m.a.s.l. 67% of the ~17 km^2 catchment consists of subalpine meadow and spruce-fir forests, but the remaining area is either sparsely vegetated or unvegetated.

Gauging stations were installed in the spring, and removed in the fall of each year. Each gauging station was equipped with a pressure transducer (Keller Series 169). Water pressure was sampled at 10 second intervals and hourly and daily averages were recorded using a Campbell CR10 datalogger. The pressure record was converted to a discharge hydrograph using rating curves. Discharge was measured by the velocity-area method, and at least 10 discharge measurements were used to fit the rating curve function. The error associated with the discharge is estimated to be +/-10% (Dingman, 1993). Air temperature and rainfall were measured at a meteorological station near the outflow of the lake (Figure 2.1). Air temperature, measured using a Campbell Scientific Model 107 probe with radiation shield, was sampled every 10 seconds and averaged hourly and daily. Hourly and daily rainfall totals were measured using a tipping bucket rain gauge (Texas Electronics model TE525). Snowpack accumulation and melt were recorded using an ultrasonic depth gauge (Campbell Scientific model UDG 01).

Difficulties with the power source at the weather station in the summers of 1997 and 1998 resulted in gaps in the temperature and precipitation records. A total of 17 days of data were lost in 1997 (Days 222-232, 234-236, and 239-247) and a total of 42 days of data were lost in 1998 (Days 167-178, 201-209, 221-232, 235-247). The missing data were interpolated using linear regression equations obtained by establishing a relationship between the Bow Lake data (1940 m.a.s.l., 51°39N, 116°27E) and data from a station (operated by Alberta Environment) located less than 5km away, at Bow Summit (2080 m.a.s.l., 51°42N 116°28E) (Figure 2.1). Hourly and daily mean values were predicted for temperature. Only daily totals were predicted for precipitation since the hourly records from the two sites were poorly correlated. For the hourly mean temperature, regressions were calculated using all available points for months where data were missing. For daily mean temperature and total precipitation, regressions were calculated using all the points from June to August ($0.80 < r^2 < 0.95$). All regressions were significant at p=0.01 or better (Appendix 1).

2.3 METHODS

2.3.1 Wavelet Analysis

The wavelet analysis in this paper follows the methods of Torrence and Compo (1998). The software used was provided by C. Torrence and G. Compo, and is available at URL: http://paos.colorado.edu/research/wavelets/. Although the basic components and methods of wavelet analysis are reviewed here, readers are referred to Torrence and Compo (1998) for a more detailed explanation of the analysis.

2.3.2 The continuous wavelet transform and wavelet functions

The wavelet transform was designed to analyse time series that contain non-stationary power over many different frequency scales (Daubechies, 1990) and is most easily understood when compared to the more commonly used Fourier Transform. The Fourier transform breaks up a signal into sine waves, and expresses a signal in terms of the frequency (x) and power (y) of its constituent sine waves, without reference to when the frequencies occur. Localisation in time can be achieved with the Fourier transform by transforming the data within a specified window of time and shifting this window along the time series (Daubechies, 1992). However, the window length has to remain fixed regardless of the frequency. The *wavelet transform* addresses this problem by breaking up a signal into scaled versions of a *wavelet function*, where the scale of the wavelet (the window) varies with frequency. Thus, the wavelet is narrow in time at high frequencies and the scale of the wavelet increases with decreasing frequency. The wavelet transform therefore expresses a time-series in 3 dimensional space: time (x), scale/frequency (y), and power (z).

The wavelet transform may be continuous where the transform is calculated for all scales and positions in time, or discrete where the transform operates on discrete dyadic scales and positions in time. The continuous transform is used in this study. The *continuous wavelet transform* of a discrete time series, x_n, is defined as:

$$W_n(s) = \sum_{n'=0}^{N-1} x_{n'} \psi^* \left[\frac{(n' - n)\delta t}{s} \right] \tag{1}$$

where N is the number of points in the time series, $\psi(t)$ is the wavelet function (normalised to have unit energy) at scale s and translated in time by n, δt is the time step for the analysis, and * indicates the complex conjugate (Torrence and Compo, 1998). Equation (1) is therefore the convolution of x_n with a scaled and translated version of the wavelet function. However, the calculation of the wavelet transform is much more efficient if the convolution is done in Fourier space using the Fourier Transform (Torrence and Compo, 1998):

$$W_n(s) = \sum_{k=0}^{N-1} \hat{x}_k \hat{\psi}^* (s\omega_k) e^{i\omega_k n\delta t} \tag{2}$$

where $\hat{x}_k$ is the Fourier Transform of x_n, k is the frequency index (0..N-1), $\psi(s\omega_k)$ is the Fourier Transform of the wavelet function at scale s and angular frequency ω_k.

A *wavelet function* is a waveform that has a zero mean and can be localised in both time and frequency space (Misiti et al., 1996). Numerous wavelet functions exist, and the choice of a function depends on both the desired analysis and the nature of the time-series being analysed. Wavelet functions can be either orthogonal or non-orthogonal, and they can be complex or real valued functions. Orthogonal wavelets can only be used for discrete wavelet analysis, while non-orthogonal wavelets can be used for either discrete or continuous wavelet analysis. If the analysis requires information about the phase relationship between the wavelet spectra of two series, a complex wavelet (with a real and imaginary part) must be used. Two other aspects that should be considered when choosing a wavelet function are the width and the shape of the function. The shape of the function should reflect the features present in the data series (Smith et al., 1998; Torrence and Compo, 1998), and the width of the wavelet will depend on whether one is looking for good resolution in time or in frequency (Torrence and Compo, 1998). The work presented in this paper uses the Morlet wavelet:

$$\psi(t) = \pi^{-1/4} e^{i6t} e^{-t^2/2} \tag{3}$$

The Morlet wavelet, as shown in Equation 3, is the equation used by Torrence and Compo (1998). It is non-orthogonal and complex.

2.3.3 Local wavelet spectrum (variance) and cross-wavelet spectrum (covariance)

The *local wavelet power spectrum* (Torrence and Compo, 1998), is defined as the squared absolute value (or squared amplitude) of the wavelet transform coefficients ($|W_n(s)|^2$). The square of the absolute value ($|z|^2$) of a complex number ($z = a + bi$) is simply the product of the number and its complex conjugate ($z \cdot z^* = (a+bi)\cdot(a-bi) = a^2 + b^2$). Therefore, the *local wavelet power spectrum* is expressed as:

$$W_n^{XX}(s) = W^X(s) W^{X*}(s) = \left|W_n^X(s)\right|^2 \tag{4}$$

where, again, the asterisk denotes the complex conjugate. When the wavelet function is complex (e.g. the Morlet), the wavelet transform coefficients are also complex. The values of the wavelet spectrum represent the magnitude of the variance in the series at a given wavelet scale and location in time.

When comparing two series x_n and y_n, the *local cross-wavelet spectrum* (or covariance) of the two series can be determined:

$$W_n^{XY}(s) = W_n^X(s) W_n^{Y*}(s) \tag{5}$$

Another useful property of the cross-spectrum of two series is the *phase difference* between the two series:

$$\theta_n^{XY}(s) = \tan^{-1}\left(\Im\{W_n^{XY}(s)\} / \Re\{W_n^{XY}(s)\}\right) \tag{6}$$

where $\Im\{W_n^{XY}(s)\}$ and $\Re\{W_n^{XY}(s)\}$ are the imaginary and real parts of the cross-wavelet spectrum, respectively (Torrence and Compo, 1998). The phase is given in degrees (0-180), where an 180° phase difference means the two series are completely out of phase. Therefore, at a scale of 24 h, the dependent variable lags the independent variable by 12 h.

Since the wavelet spectrum presents a large amount of information in one image, it is often desirable to condense this information by averaging the results over a range of scales or times. One useful technique is to average the variance at every scale over the whole time series, to compare the spectral power at different scales. Torrence and Compo (1998) call this the "global wavelet spectrum". The result is a graph of variance vs. scale, analogous to the Fourier power spectrum, in which localisation in time is lost. The ***global wavelet spectrum*** is defined as:

$$\overline{W}_n^{XX}(s) = \frac{1}{N}\sum_{n=o}^{N-1} W_n^{XX}(s) \tag{7}$$

where N is the length of the series x. It is also often desirable to extract the results for a single wavelet scale, especially if the wavelet power is located in a limited number of scales.

2.3.4 Significance Levels

The significance of the wavelet power spectrum can be evaluated by comparing the spectra to a background (or noise) spectrum. The background spectrum depends on the nature of the data. In geophysical processes the background spectrum is often either white noise (constant variance across all scales, or frequencies) or red noise (increasing variance with increasing scale, or decreasing frequency; Schiff, 1992; Torrence and Compo, 1998). Once the background spectrum is chosen, the wavelet spectrum of the time series is compared to the expected spectrum of the background function at a determined confidence level. Where the wavelet power of the time series exceeds the power of the background at the chosen confidence level, the time series variance can be deemed significant relative to the expected background. The calculation of the background spectrum depends on the type of wavelet spectrum being evaluated: local, global, or cross spectrum (Torrence and Compo, 1998). For example, the distribution of the normalised local wavelet power spectrum is:

$$\frac{W_n^{XX}(s)}{\sigma_x^2} \Rightarrow \frac{1}{2} P_k \chi_2^2 \tag{8}$$

at each time *t* and scale *a*. Where the value of P_k is the mean Fourier power of the background spectrum for the Fourier frequencies *k* that correspond to the wavelet scales *s*, and χ^2_2 is chi-square value for the chosen confidence level (e.g. 95%), where the subscript '2' on χ^2 designates the degrees of freedom (2 for a complex wavelet and 1 for real valued functions). The Fourier power (P_k) of white noise spectrum is equal to 1 at all *k*. For the red noise spectrum, the Fourier spectrum is (Torrence and Compo, 1998):

$$P_k = \frac{1-\alpha^2}{1+\alpha^2 - 2\alpha\cos(2\pi k/N)} \qquad (9)$$

where α is the assumed lag-1 autocorrelation for the time series.

The next section explains how the wavelet analysis tools described above were applied to the data collected at Bow Lake between 1997-2000.

2.3.5 Wavelet analysis of discharge and temperature time-series

The Morlet wavelet was chosen for this analysis, because it is complex and thus allows for the determination of the phase relationship between the temperature and discharge series. The Morlet wavelet also has relatively good resolution in frequency compared to other wavelets, such as the Mexican Hat or Paul, which have better resolution in time. Furthermore, the wavelet is smooth and symmetrical, similar to the features in the temperature and discharge time series. It has also been used previously in both hydrological and meteorological applications (Labat et al., 2000; Torrence and Compo, 1998)

The start date and total length of the stream discharge and temperature measurements varied from year to year. To simplify inter-annual and inter-stream comparisons of the wavelet analyses, the time series were truncated to keep the start and end dates consistent. The series were confined to the latest start date (June 7th, day 157), and the earliest end date (September 3rd, day 247) for a total series length of 2130 h, or 88.75 days. The only exception to this is the 1997 hourly temperature record, which ends on August 30th, 1997. Since the temperature and discharge time series have widely different statistics, the series were also centred on their means and normalised by their standard deviations prior to calculating the wavelet transforms to facilitate comparison of results across catchments and years. The hourly precipitation data from 1999 and 2000 were not normalised because the large number of zeros in these time series meant that the data were not normally distributed.

The wavelet transform was calculated for a discrete set of 42 ($j = 0, 1 \ldots 41$) scales. The scales are a series of fractional powers of two (Torrence and Compo, 1998):

$$s_j = s_o 2^{j\delta j} \qquad (10)$$

where $s_o = 6$ h and $\delta j = 0.125$. This gives scales ranging from 6 h to 209 h (approximately 9 days). It should be noted that the wavelet scale is often expressed in terms of its equivalent Fourier Period in order to facilitate the comparison of the wavelet and Fourier power spectra. The scale/period relationship varies for different wavelet functions, and the equivalent Fourier Period for a particular wavelet can be derived analytically (Torrence and Compo, 1998). For the Morlet wavelet the wavelet scale and Fourier Period are almost equal (period = 1.03*scale), so the terms period and scale are used interchangeably here.

The red-noise spectrum was chosen as the background spectrum for testing the significance of the results, since the data match this spectrum quite well. A lag-1 autocorrelation coefficient (α in Equation 9) of 0.96 was found for all 4 temperature series (1997-2000), but α values for the runoff time series varied between each year. Their values are presented in Table 1. For the wavelet analysis of rainfall a white noise spectrum was used as the background ($\alpha = 0$).

The local wavelet power spectra ($W_n^{QQ}(s)$ *or* $W_n^{TT}(s)$), the global wavelet spectra ($\overline{W}_n^{QQ}(s)$ *or* $\overline{W}_n^{TT}(s)$), and the corresponding 95% confidence levels for the red-noise spectra were determined for each of the discharge series (4 for the Glacial stream (Q_{GL}) and 4 for the Bow River (Q_{BR})) and temperature series (T) for the summers (June-August) 1997 to 2000. The local wavelet cross-spectra ($W_n^{TQ}(s)$) and the phase coherence ($\theta_n^{TQ}(s)$ or lag) were then determined for the paired temperature (independent variable) and runoff (dependent variable) series for each year. The local precipitation-runoff wavelet cross-spectra ($W_n^{PQ}(s)$) and the phase coherence ($\theta_n^{PQ}(s)$) were also determined for 1999 and 2000.

2.4 RESULTS

A summary of seasonal snow, temperature, and rainfall conditions illustrates the inter-annual variability in the gross hydroclimatological conditions at Bow Lake in the period 1997-2000 (Table 2). The year fall 1997 to fall 1998 had much lower snowfall, and higher spring and summer temperatures than all the other years. According to monthly snow course measurements at Bow Summit by Alberta Environment (Figure 2.1), the snow accumulation (mm-SWE) at the end of March 1998 was approximately 57% of that in March 1997, 1999 and 2000. The positive degree-day total (Jan 1- Sept 3), a measure of energy input during the melt season, was 26-30% higher in 1998 than in the other years. 1999 was the coldest summer, and winter 1998-99 had the highest snowpack SWE. In 1998 the Glacial stream had the highest total seasonal runoff of the four years (3.4×10^7 m^3), while the Bow River had the lowest total runoff that year (4.1×10^6 m^3). In the case of the Bow River, seasonal runoff increased with increasing snowpack SWE (Table 2). For the Glacial stream seasonal discharge increased with increasing temperature (positive degree-day total) and decreasing snowpack (SWE) (Table 2).

Figure 2.2 and Table 2.3 present the results of the global wavelet analysis of the discharge and air temperature time series for 1997-2000. The power of the global wavelet spectra is the variance averaged at each scale across the whole length of the time series. Since the data series were mean centred and normalised, the spectral power is dimensionless. Therefore, the wavelet *power* expresses the *variance of the series* as squared standard deviations from the mean. The terms variance and power are used interchangeably in the text. The 95% confidence level for a red noise spectrum (the significance line) was determined for each spectrum. In order to avoid cluttering the graphs, only the significance lines for the 1997 (α_{GL}= 0.93 and α_{BR} = 0.97) and 2000 (α_{GL}= 0.999 and α_{BR} = 0.997) series were plotted. The α values are highest for 2000 because the signal is very smooth, and the autocorrelation of the data is very strong at a 1h lag. The lower α values for 1997 indicate that the discharge signal is noisier than for other years (Table 1). As a result the significance lines for the background spectrum in 1997 are higher than in other years, and the variance in the discharge series has to be much stronger in order to be considered significant.

The power around the 24 h scale is the dominant feature in all the global spectra, indicating strong diurnal signatures in the time series. There is also high power at low frequency (96 < 192 h) in all years, indicating strong signals at the scale of weather systems (4-8 days), but the power is not usually significant at these scales (Figure 2.2, Table 2.3). For the Glacial stream, the diurnal signal was strongest in 1998 and then 1997 (Figure 2.2 a, Table 2.3). In 1999 and 2000 the power of the diurnal signal was orders of magnitude lower than in 1998. The wavelet power at the 12 h scale was also significant for the Glacial stream runoff in 1998 (Figure 2.2 a). For the Glacial stream the mean low frequency global power centred on 120 h ($\overline{W}_n^{QQ}(120)$), was greater than the 24 h scale power $\overline{W}_n^{QQ}(24)$in all years except 1998 (Table 3). The magnitude of the diurnal and low frequency power was always higher for the Glacial stream than for the Bow River (Table 3). This implies that the Glacial stream discharge is more responsive to temperature changes, both at diurnal timescales and at the scale of weather systems.

The distribution of global power across scales is similar for the two streams, but the magnitude of the power is much lower for the Bow River (Figure 2.2 b). The global diurnal power for the Bow River runoff was most pronounced in 1997, followed by 1999 (Table 3). However, despite the magnitude of the power, the global variance in the Bow River runoff at the 24 h scale was not statistically significant in 1997, due to the noise in the record (Figure 2.2 b). The 12 h scale variance in runoff was significant for this stream in 1998, 1999 and 2000. The average low frequency power for the Bow River was generally of the same order of magnitude as the diurnal scale power, and was lowest in 1998 (Table 2.3). The global wavelet spectra for temperature are similar to the stream discharge spectra, but the power is orders of magnitudes higher (Figure 2.2 c, Table 2.3). The power is very strong at the 24 h scale, and there is little variability from year to year. The power is also strong at low frequencies, where it displays greater inter-annual variability (Figure 2.2 c, Table 2.3).

The temperature and discharge time series are shown in Figures 2.3-2.6 along with their local wavelet spectra. The significant features of the wavelet analyses are also summarised by stream and year in Table 2.4. As for the global spectra, most of the variance in the local spectra is concentrated at the 24 h scale, although periodically there is significant variance at sub-diurnal scales (Figures 2.3, 2.6 a-c(ii)) and also at higher scales (Figures 2.3 c(ii), 2.5 a(ii) and 2.6 a(ii)). For the Glacial stream, the low frequency power (>96 h) is usually strongest in July and August (Figures 2.3 a(ii)-2.6 a(ii)). For the Bow River discharge, the power at low frequency is strongest in June and early July, but is never statistically significant, and always much lower than for the Glacial stream discharge (Figures 2.3 b(ii)-2.6 b(ii)). The diurnal component of the local wavelet spectra for air temperature is much more consistent in strength and distribution in time than the low frequency power (e.g. Figure 2.3 c(ii)). The diurnal power for the discharge spectra is much weaker than for air temperature, and there is greater seasonal and inter-annual variability in the distribution of the 24 h discharge signal (Figures 2.3-2.6).

In 1997, the local wavelet spectra for runoff in both streams had significant power at the 24 h and 6-12 h scales near the beginning of June (Figures 2.3 a(ii) and 2.3 b(ii), day 158-170). This power increased moderately in both streams between the end of July and end of August but it was not significant (Figures 2.3 a(ii) and 2.3 b(ii), day 195-240). In 1998 the 24 h wavelet power for discharge in both streams was concentrated between mid July and August, with frequent episodes of significant power at the 6 and 12 h scales, especially in August (Figure 2.4 a(ii) and 2.4 b(ii), day 190-248). The power in the diurnal discharge cycle was always higher in the Glacial stream than in the Bow River in 1997 and 1998 (Figures 2.3 and 2.4, 2.7 d and 2.8 d).

In 1999 and 2000 the diurnal signal in Glacial stream discharge was much weaker than in 1997 and 1998, but the variance was still statistically significant, especially during July and August (Figure 2.5 a(ii), day 210- 240, Figure 2.6 a(ii) day 190-220). In 1999 the 24 h power in the Bow River was highest in June and again at the end of August (Figure 2.5 b(ii)), and in 2000 it was strongest in early June and then increased occasionally, particularly during July (Figure 2.6 b(ii)).

The local temperature-runoff cross-wavelet spectra mimic the general patterns present in the local wavelet spectra for discharge (Figures 2.7-2.10). Since the temperature consistently displays strong variance at the diurnal scale in the local spectra, the seasonal and inter-annual variability in the local temperature-runoff cross-wavelet spectra is a lot lower than in the local spectra of the discharge series. The local cross-wavelet spectrum can have significant coherence in places where only one of the paired local wavelet spectra displays a significant signal (e.g. compare Figures 2.7 and 2.3). Hence the local cross-wavelet spectra and the corresponding local wavelet spectra should be examined together, to determine whether the 'significant' covariance is actually meaningful in terms of the runoff variance. The significance contours for local wavelet power in the discharge series are therefore plotted on each of the local cross-wavelet spectra to show when the strong temperature-discharge covariance coincides with significant variance in stream runoff. The phase difference at the 24 h scales is shown in Figures 2.7c-2.10c.

In general the temperature-discharge covariance for both streams is concentrated at the 24 h timescale, and sometimes at shorter timescales (Figures 2.7-2.10). There is also strong covariance at higher scales for the Glacial stream (Figures 2.7 a, 2.9 a, and 2.10 a). When discharge showed strong variability at the 24 h and higher scales, it was usually strongly co-variant with temperature (Figures 2.7 a,b-2.10 a,b). However, at shorter (2.6-2.12 h) timescales, discharge often showed strong variability in the absence of strong covariance with temperature. This was especially true for the Bow River in 1999 (Figure 2.9 b, day 196, 227-248) and 2000 (Figure 2.10b, day 158-164, 188, 198, 205), and for both streams in 1998 (Figure 2.8a-b, day 210-225). These episodes of high variance in discharge at the lower scales appear to be related to precipitation events.

The phase difference between temperature and discharge at the 24 h scale was typically between 4-6 h (60°-90°) and the Bow River discharge usually responded more quickly to temperature than the Glacial stream, except in 1999 (Table 2.4). The phase differences for the two streams were very similar in 1997, when they did not exceed 6 h, and only fell below 4 h on one occasion (Figure 2.7 c). In 1998 the phase differences for the two streams were less similar

(Figure 2.8 c), and the average phase differences for both streams were shorter than in all other years (Table 2.4). The lags were higher for both streams, between 6-9 h, for most of 1999 (Figure 2.9 c, day 160-230) and 2000 (Figure 2.10 c, day 160-215). The difference in lags between the two streams in 1999 was small until the end of August, when the Glacial stream had a faster response (Figure 2.9 c, day 228-248). In 2000, the Bow River discharge usually had shorter lag times than the Glacial stream, especially in June (Figure 2.10 c, day 160-188). Another key feature of the phase difference graphs is the irregular, sudden and dramatic changes (Figures 2.7 c-2.10 c). These large drops and/or increases in lag were generally short lived and appeared to coincide with precipitation events. They were more frequent and more pronounced for the Bow River than for the Glacial stream.

The abrupt disruptions in the phase diagrams led to the investigation of precipitation-discharge relationships. Since the hourly precipitation records for 1997 and 1998 were discontinuous, the wavelet analysis of precipitation data was performed only for 1999 and 2000. The local wavelet spectra for precipitation and the local discharge-precipitation cross-wavelet spectra are illustrated in Figures 2.11 and 2.12. As for the discharge-temperature cross-spectra, the significance contours for local wavelet power of the discharge series are plotted on the discharge-precipitation cross-wavelet spectrum to illustrate when variance in discharge was significant. In addition, the local wavelet power for discharge and precipitation at the 24 h scale is plotted below the local cross wavelet spectra (Figures 2.11 e and 2.12 e).

Unlike the local discharge and temperature spectra, where the power is concentrated at the 24 h scale, the power in the local rainfall spectra is spread out across the 6-192 h scales depending on the duration of the event. There were more major precipitation events in 1999 than in 2000 (Figure 2.11 b and 2.12 b). Compared to the Bow River, the Glacial stream shows little or weak covariance with precipitation (Figures 2.11-2.12). The response of the Bow River discharge to precipitation events appeared to be delayed by 1 or 2 days in June and early July (Figure 2.11 d, day 183-188 and Figure 2.12 d, day 160-165, 185-188), but not later in the summer.

2.5 DISCUSSION

2.5.1 Conceptual model for the interpretation of wavelet analyses

In glacial and nival catchments, spatial and temporal changes in water sources, and in hydrological storage and transfer processes occur as a result of seasonal snow and ice melt.

These seasonal changes in the hydrological system manifest themselves as changes in characteristics of the discharge hydrograph, and also as changes in the relationship between air temperature and discharge. The following discussion outlines the typical seasonal changes in the hydrologic processes in the two types of catchment, and the features in the time series and wavelet analyses that can be used to identify shifts in hydrologic behaviour.

Within a catchment there are seasonal changes in the relative contribution of different water sources to runoff. In an ice-free catchment, the dominant component of runoff shifts from snowmelt to rainfall and base flow. In a glacial catchment, snowmelt continues at higher elevations and is replaced by ice melt in the ablation zone, and by rainfall in ice-free areas. Changes in storage and flow routing also occur as snowmelt progresses. Early in the season meltwater percolates into the snowpack and is stored or refrozen. Once the snowpack ripens, meltwater runoff begins. As the snowpack thins, the time required for meltwater to percolate from the melting surface to the base of the snowpack decreases (Fountain, 1996). At the start of the season, overland flow may be common over soils that are frozen at shallow depth. If soils thaw from the top down, storage capacity gradually increases but deep flow paths are sealed off by pore ice at depth. Shallow subsurface and overland flow result as soils thaw and receive inputs from snowmelt and precipitation. This may continue until the ice at depth melts, and deep flow paths open. In a glacial catchment the exposure of low albedo ice and the resulting increase in the melt rate leads to the seasonal development of more efficient supraglacial, englacial and subglacial drainage pathways (Richards et al., 1996). As a result, the glacial system becomes more responsive to meltwater inputs, especially later in the summer if major subglacial channels develop. The rapid response of the glacial system in 1998 is indicated by the strong power at the 12 h time scale (Figure 2.4). However, in the case of runoff from Bow Glacier, the proglacial lake is a potentially large storage reservoir (volume 9×10^6 m^3) that may dampen the variability of runoff from the glacier (Figure 2.1).

The seasonal changes in the dominant water sources, and storage and flow routing processes discussed above, can be identified using various features of the raw time series and wavelet analyses. The retreat of the seasonal snowpack in an ice-free catchment should result in a decrease in the amplitude of the diurnal discharge signal, a decrease in the responsiveness of discharge to longer scale (4-8 day) temperature variability, and a recession of the discharge hydrograph. Therefore, in a snowmelt fed catchment the retreat of the snowpack should be indicated by a decrease in the wavelet power ($W_n^{QQ}(s)$) at 24 h and low frequency scales, and a drop in discharge below the seasonal mean (when the normalised discharge drops below zero).

The loss of the snowpack as a storage reservoir might also be indicated by a decrease in the phase difference between the temperature and discharge signals at diurnal scales, since the travel time of meltwater to the stream should decrease. Since the exposure of glacier ice amplifies the response of discharge to temperature variations, this event should be marked by a significant increase in the daily mean discharge, increases in the wavelet power at diurnal and longer timescales, and by an increase in the temperature-discharge cross-wavelet covariance for the Glacial stream. The development of major channels in the glacier system may lead to further increases in the wavelet power for discharge at 24 h and shorter timescales, as well as decreases in the lag between diurnal temperature and discharge cycles, due to the faster transfer of meltwater and rainfall runoff from ice surfaces (Fountain, 1996).

Discharge response to rainfall is indicated by sudden changes in the temperature-discharge phase difference. It is also shown by the presence of significant power in the discharge wavelet spectra that is not associated with significant covariance in the temperature-discharge cross-spectra (this implies that the discharge variability is not due to temperature induced meltwater runoff, but to a non-melt water source such as rainfall). The type of precipitation is also important, as summer snowfalls may drastically reduce the melt response of old snow and glacier ice for periods of several days (Fountain, 1996).

Changes in the type of flow routing in a catchment, such as a switch from shallow subsurface flow to overland flow of melt water due to the saturation of soils, are more difficult to identify using the wavelet analyses. However, a delay between the peak temperature-discharge covariance, or the precipitation-discharge covariance, and the peak in the wavelet power for discharge suggests that the meltwater or precipitation is being retained in the snow and/or soils before being routed to the stream (Figure 2.10 b, day 160-164; Figure 2.12 d day 160-164, 186-188). On the other hand the overland flow routing of rain or meltwater may be indicated by strong short scale (6-12 h) wavelet power for discharge that coincides with a precipitation event (Figure 2.8 b, day 167).

2.5.2 Interpretation and evaluation of the results

The inter-annual variations in air temperature and snowfall conditions at Bow Lake (Table 2.2) can largely be explained by the 1998 El Niño event and the strong La Niña conditions that followed in 1999 and 2000. The Southern Oscillation Index (SOI) anomaly for 1951-2000 (Figure 2.13) illustrates that 1997-1998 was one of the strongest El Niño events on record, and

1999 and 2000 experienced relatively strong La Niña conditions. The west coast of Canada and the U.S. typically experience considerably warmer temperatures, lower snowfall, and lower stream flows in the year following the onset of El Niño (Brown, 1998; Kahya and Dracup, 1993; Kiladis and Diaz, 1989; Redmond and Koch, 1991). At Bow Lake the low snowfall in 1997-98, combined with the high spring and summer temperatures in 1998, led to the early disappearance of snow from the catchments. This resulted in low seasonal discharge in the Bow River, but higher discharge in the Glacial stream.

The results of the wavelet analyses highlight the unique hydrological regime brought on by the 1998 El Niño conditions. The early removal of snow from the catchments in 1998 is indicated by the fall of the normalised discharge in the Bow River below zero as early as day 195 (Table 2.3). The low global wavelet power around the 120 h scale for the Bow River also illustrates that this stream was less responsive to weather related melt forcing in 1998, as a result of the thin snowpack (Table 2.3). The global power at the 12 and 24 h scales for the Glacial stream was double the power at these scales in other years, probably a result of the extensive exposure of glacial ice in 1998 (Table 2.3). Table 2.3 also shows that the diurnal scale power for the Bow River and the Glacial stream increased together for 1997, 1999 and 2000. In 1998, however, the 24 h power for the Bow River discharge was relatively low and the 24 h power for the Glacial stream was at a maximum. The ratio of global 24 h power in the two streams (GL/BR) versus the diurnal scale global power for the Glacial stream ($\overline{W}_n^{QQ}(24)$GL) also illustrates the dramatically different relationship between runoff in the two streams in 1998 (Table 2.3). These results indicate that snowmelt was the dominant runoff source in the two streams in 1999 and 2000, and to a lesser extent in 1997. In 1998, the removal of snow from the catchments resulted in an exponential increase in the diurnal discharge response in the Glacial stream due to significant ice melt, and a sharp reduction in response in the Bow River due to the complete and early removal of the snowpack.

The strong and persistent 12 h scale power in the Glacial stream discharge wavelet spectrum during July and August 1998 (Figure 2.4 b(ii), day 215-247) indicates that the exposure of glacial ice probably led to the development of major channels within the glacial drainage system late in the summer. The persistence of the short scale power in the glacial discharge signal strongly suggests that the signal is due primarily to an expansion of the drainage system as opposed to transient extreme floods from melt or precipitation (Rothlisberger and Lang, 1987). The shift in the phase lag from approximately 110° (7 h) to 70° (4.5 h) around day 190 in 1998 is also an indication of the exposure of glacial ice and/or the development of subglacial channels. The increase in the phase difference in the Glacial stream around the same time that the 12 h discharge signal gained strength (Figure 2.8 c, day 220-247) may seem to challenge this suggestion. However, there was a strong inverse relationship between the phase difference and the time of daily maximum air temperature for both streams during this period (Figure 2.14 a), which indicates that the increase in lag was due to air temperatures peaking earlier in the day. Such a shift in the time of the daily air temperature peak was not observed at any other time in the four years of study. The air temperature for Bow Lake was estimated from the Bow Summit weather station for virtually all of this period (day 221-232, 234-247). Therefore, the increase in the phase difference at the end of the season in 1998 was most likely a result of a difference in the timing of the daily air temperature peaks at the 2 sites, rather than a change in runoff response. Figure 2.14 b confirms that, between day 215-247, the time of peak discharge was generally constant.

In July and August 1997, there was an increase in the discharge and the 24 h power for the discharge wavelet spectra for the Glacial stream. However, the power at the 24 h scale was much weaker than in 1998 and there was no evidence of any variability in discharge at lower scales (Figure 2.3 a(i), (ii)). This suggests that some ice was exposed on the glacier in that year, but that the degree of exposure was not nearly as extensive as in 1998, and that there was little development of the subglacial drainage system. Compared to 1999 and 2000, the low phase difference between air temperature and stream discharge in 1998 and 1997 (Table 2.4), indicates that the snowpack was more effective at retarding the runoff of the diurnal melt water pulse in 1999 and 2000. In 1997 and 1998, the diurnal scale variability in the Bow River discharge was maintained throughout most of the summer, with a temporal distribution of power very similar to that in the Glacial wavelet spectra (Figure 2.3 and 2.4). This persistent diurnal cycle in the Bow River catchment indicates a continuing input of melt runoff from the small area of ice cover in the catchment in these years. This ice melt source only appears to have contributed significantly to Bow River runoff in years when the previous winter's snowpack was thin and/or summer temperatures were high (Table 2.2). In 1999 and 2000, variability in the Bow River discharge at the 24 h scale was very low or absent through most of July and August, when the diurnal runoff signal gained strength in the Glacial stream (Figure 2.5 and 2.6).

The frequent significant variability in discharge at the lower scales (<24 h), and rapid changes in discharge-temperature phase difference for the Bow River, suggest that precipitation is a more important component of runoff and follows more direct flow routes in the Bow River catchment than in the Glacial catchment. For example, between day 160-205, 2000, the phase difference for the Bow River showed several short-lived dramatic shifts. The Glacial stream lags changed at approximately the same time as those for the Bow River, but the shifts were less pronounced in the Glacial stream (Figure 2.10 c). For the Bow River, there were also several instances of strong discharge wavelet power that were unrelated to strong temperature-discharge covariance. However, no such instances were observed for the Glacial stream (Figures 2.10 a-b, day 160-205). The covariance between precipitation and discharge was also much stronger for the Bow River than for the Glacial stream at the beginning of the season (Figure 2.12). After day 205, however, the response of discharge to precipitation was higher for the Glacial stream (Figure 2.12c-d). This implies that ice may have been exposed on the glacier or that soils in the Bow River catchment had reduced moisture content and greater storage capacity, or both.

The retardation of snowmelt routing, as indicated by the mean annual phase difference between temperature and stream discharge, generally varied with the thickness of the seasonal snow pack, and the size of the catchment. Except in 1999, the phase lags were higher for the Glacial stream than for the Bow River, and they were lowest in both streams in 1998 (Table 2.4).

By locating and quantifying the strength and significance of the variability in stream runoff at different scales, and the relationship between temperature and runoff cycles, the wavelet analyses appear to be a useful tool for comparing the relative contributions of water sources to runoff both seasonally and inter-annually. However, the wavelet analyses do not unambiguously identify changes in hydrological flow routing within the catchments. The phase difference between temperature and discharge is an indication of the relative influence of the snowpack on storage of melt water, and strong wavelet power at very short time scales (6-12 h) can indicate the influence of faster flow routes either within the glacial drainage system, or overland flow. However, it was anticipated that the wavelet analyses might help differentiate between periods of overland flow and shallow subsurface flow during the snowmelt period. Such changes are, however, no more obvious in the wavelet results than they are in the discharge hydrographs.

2.6 CONCLUSIONS

Wavelet analysis is a fast and effective tool to quantify and compare the inter-annual variability in runoff and the relationships between runoff and temperature/rainfall in glacial and nival catchments, especially when dealing with large data sets. The strong power at 12 h and diurnal scales in the local wavelet spectra for glacial runoff in 1998 indicate that significant ice exposure and the development of channelised glacial drainage occurred in 1998. This was due to the low snowfall and high temperatures at Bow Lake during the 1997-1998 El Niño event. The analyses showed that the early retreat of the snowpack, as observed in 1997 and 1998, led to a continuing input of melt runoff from a small area of ice cover in the Bow River catchment. Rainfall had a stronger influence on runoff, and followed quicker flow paths in the Bow River catchment than in the Glacial catchment. The results also illustrate that the snowpack thickness and catchment size were the primary controls on the phase difference between diurnal temperature and discharge cycles.

By quantifying the strength and statistical significance of variance in discharge, and of the covariance between discharge and temperature/precipitation forcing, at different scales of response, wavelet analysis appears to be a useful tool for identifying inter-annual and seasonal changes in the relative contributions of different water sources to runoff. Wavelet analyses can also identify general changes in the flow routing time of snow and ice melt through the catchment, but are largely incapable of identifying changes or differences in the nature of the flow routing (e.g. overland flow vs. through flow) between or within a catchment.

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Table 2.1 The lag-1 autocorrelation coefficients (α) used for testing significance of the wavelet power.

	1997	1998	1999	2000
αGL	0.93	0.98	0.99	0.999
αBR	0.97	0.99	0.99	0.997

Table 2.2 Comparison of seasonal snowpack, temperature, and precipitation conditions at Bow Lake for 1997-2000.

	1996-97	1997-98	1998-99	1999-2000
Snowpack (mm SWE) at Bow Summit (2080 m.a.s.l.)				
30 March	462	257	460	434
30 May	254	0	329	239
Exhaustion of snowpack at Bow Lake met. station (1940 m.a.s.l.)	--	2-May	30-May	23-May
Discharge (10^6 m^3)				
Bow River (June 7-Aug 31)	7.7	4.1	8.1	7.5
June	3.5	1.9	2.9	2.5
July	2.7	1.8	3.5	3.6
August	1.5	0.9	1.8	1.4
Glacial (June 7-Aug 31)	28	34	20	19
June	9.0	5.3	3.5	2.7
July	9.3	15	6.7	8.9
August	9.4	13	9.5	7.1
Degree Day Total (°C) Jan-Aug	838	1148	791	808
Mean Daily Air Temp (°C)				
May	2.4	5.5	0.9	1.3
June	6.1	6.8	5.3	6.0
July	9.1	12.6	7.8	9.6
Aug	9.2	11.1	10.5	8.6
Total Precipitation (mm) June-August	193	233	236	155
Total monthly Precipitation (mm)				
June	59.8	82.0	27.5	41.7
July	63.4	40.4	117.1	82.8
August	69.8	110.4	91.5	30.8

Table 2.3 Summary of the global wavelet spectra for runoff (Q) and temperature (T) for the 24 h scale $\overline{W}_n^{XX}(24)$, and for the mean power centred on 120 h ($\overline{W}_n^{XX}(120)$ the average global power for scales between 96 and 148 h). The ratio of the global power for Q at the 24 h scale in the two streams is also shown ($\overline{W}_n^{QQ}(24)$GL/BR). The last column lists the day when the normalised Bow River discharge falls below zero (Q_{BR} norm < 0).

	Glacial		Bow River		Temperature		GL/BR	Q_{BR} norm
	$\overline{W}_n^{QQ}(24)$	$\overline{W}_n^{QQ}(120)$	$\overline{W}_n^{QQ}(24)$	$\overline{W}_n^{QQ}(120)$	$\overline{W}_n^{TT}(24)$	$\overline{W}_n^{TT}(120)$	$\overline{W}_n^{QQ}(24)$	< 0
1997	9.9	13	0.37	0.35	480	183	27	205
1998	20	10	0.13	0.14	370	91	154	194
1999	1.3	15	0.22	0.35	500	194	6	211
2000	0.42	3	0.08	0.33	520	117	5	216

Table 2.4 Summary of key features of wavelet analysis by stream and year. The time of occurrence of the key features are indicated by day.

Feature	1997		1998		1999		2000	
	GL	BR	GL	BR	GL	BR	GL	BR
Strong $W_n^{QQ}(24)$	160-170	160-170	162-164/ 186-248	161-165/ 187-248	167-170/ 191-193/ 210-220/ 230-243	163-170/ 179-193/ 230-247	178-184/ 189-233	160-165/ 180-189/ 195-220
Strong W_n^{QQ} (<24)	162/ 167	160-167	215-228/ 235-248	168/ 179/ 192/ 201/ 215-230/ 238		163/ 188/ 196/ 232-245	205/ 213	160-164/ 188/ 198/ 205/ 213
Significant W_n^{QQ} (>96)					203-215/ 231-247		174-245	
Strong $W_n^{QQ}(s)$, no strong $W_n^{TQ}(s)$	168		215-228/ 235-237	168/ 179/ 215-230/ 238	237-239	163/ 196/ 228-245	205-222	160-164/ 188/ 198/ 205
mean $\theta^{TQ}(24)$	5.4	4.9	5	3.6	6.3	7.4	7.1	5.6
Rapid change in $\theta^{TQ}(24)$	192-195	192-195	241-244	168-170/ 178-181/ 228-229	237-239	223-225	186-188/ 204-206	174-177/ 184-186/ 197/ 204-206

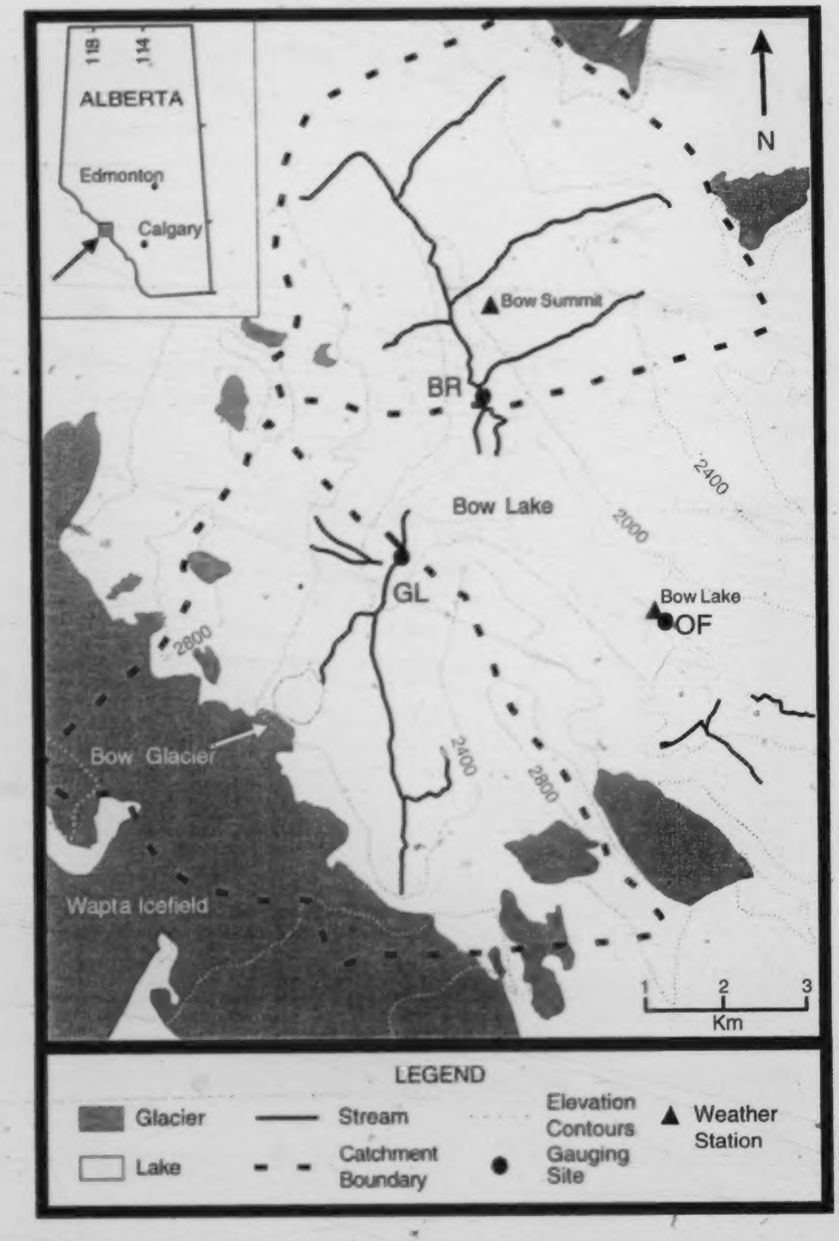
119
114
ALBERTA
Edmonton
Calgary
N
Bow Summit
BR
2400
Bow Lake
2000
GL
Bow Lake
OF
2800
Bow Glacier
2400
2800
Wapta Icefield
1
2
3
Km
LEGEND
Glacier
Stream
Elevation Contours
Weather Station
Lake
Catchment Boundary
Gauging Site

Figure 2.1 Map of Bow Lake. GL and BR mark the gauging stations for the Glacial stream and the Bow River. The Bow Lake meteorological station is located near the outflow gauging station (OF). The location of the Alberta Environment weather station at Bow Summit is also shown.

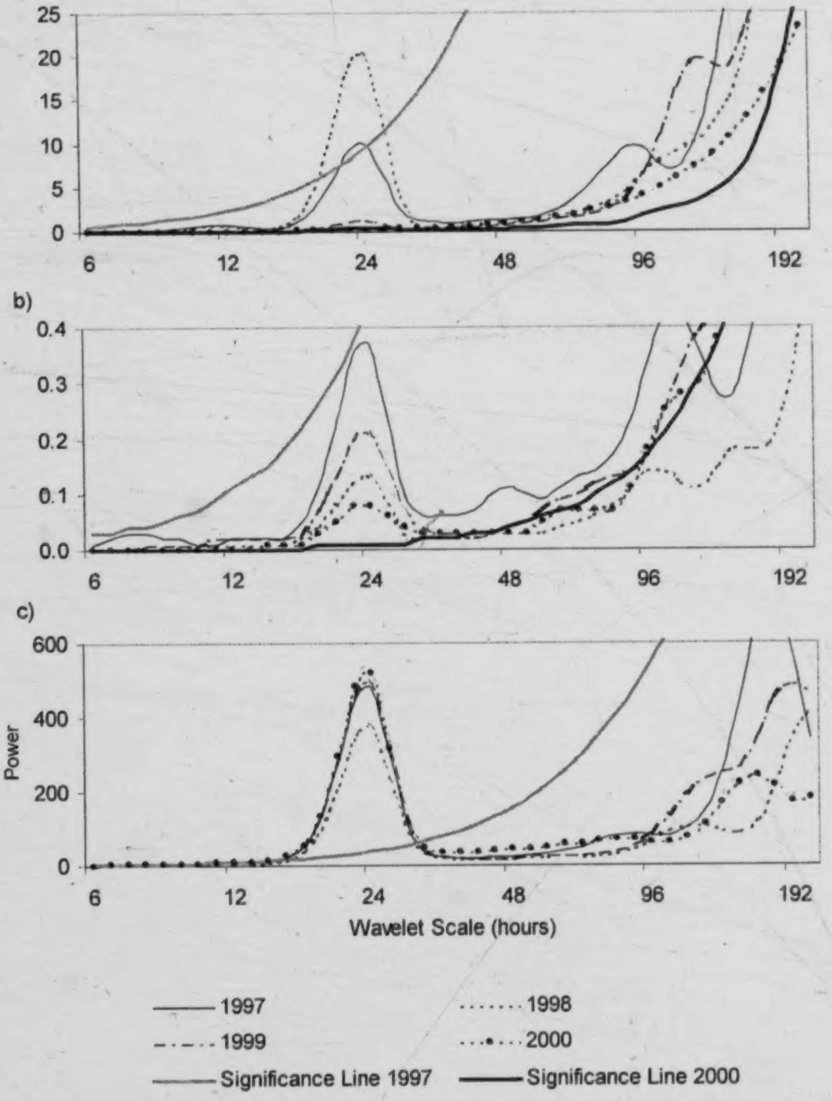

Figure 2.2 Plot of Global Spectra for each year a) Glacial stream discharge, b) Bow River discharge, c) Air temperature.

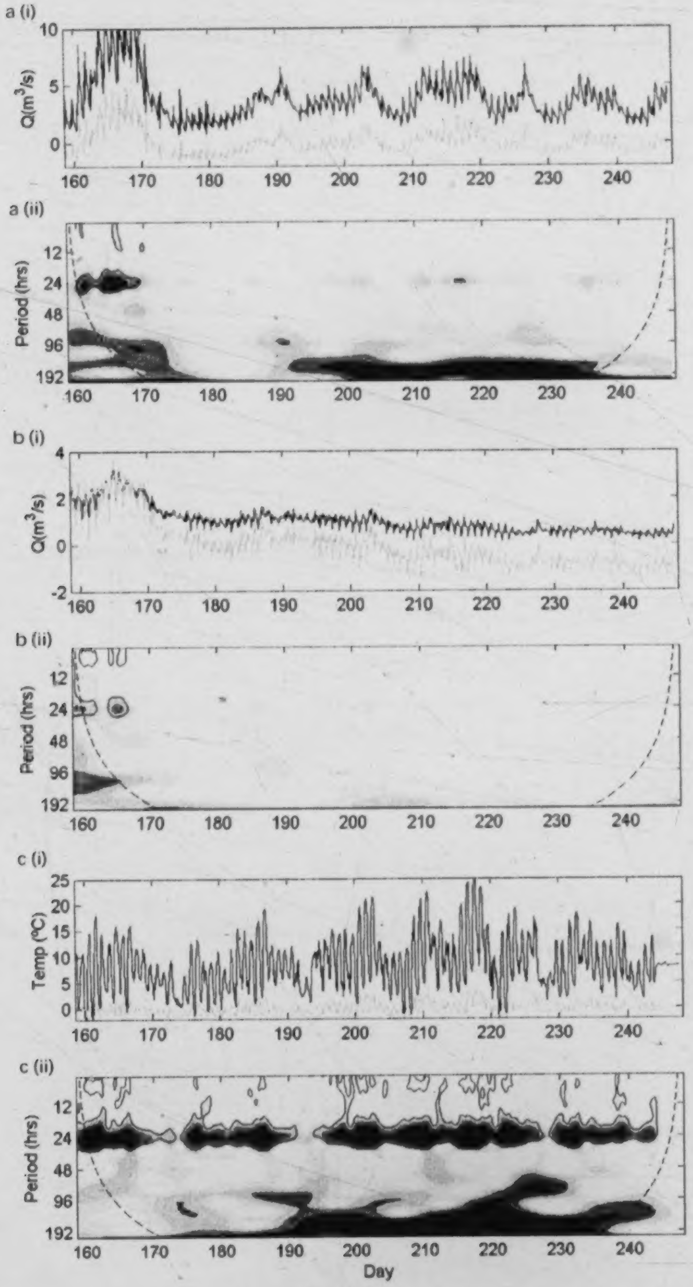

Figure 2.3 Time Series and Wavelet Spectra for 1997 (a) Glacial stream discharge (Q_{GL}) (b) Bow River (Q_{BR}) (c) Air Temperature (T). (i) The raw time series (black) and the mean centered and normalised time-series (gray). (ii) Wavelet power spectrum ($W_n^{XX}(s)$) contoured at variance 0.5, 1, 2.5, 5, 10, and 20 (light to dark gray). The black line contours areas where the power is considered significant (i.e. >95% confidence level of a red noise process), the dashed black line delineates the cone of

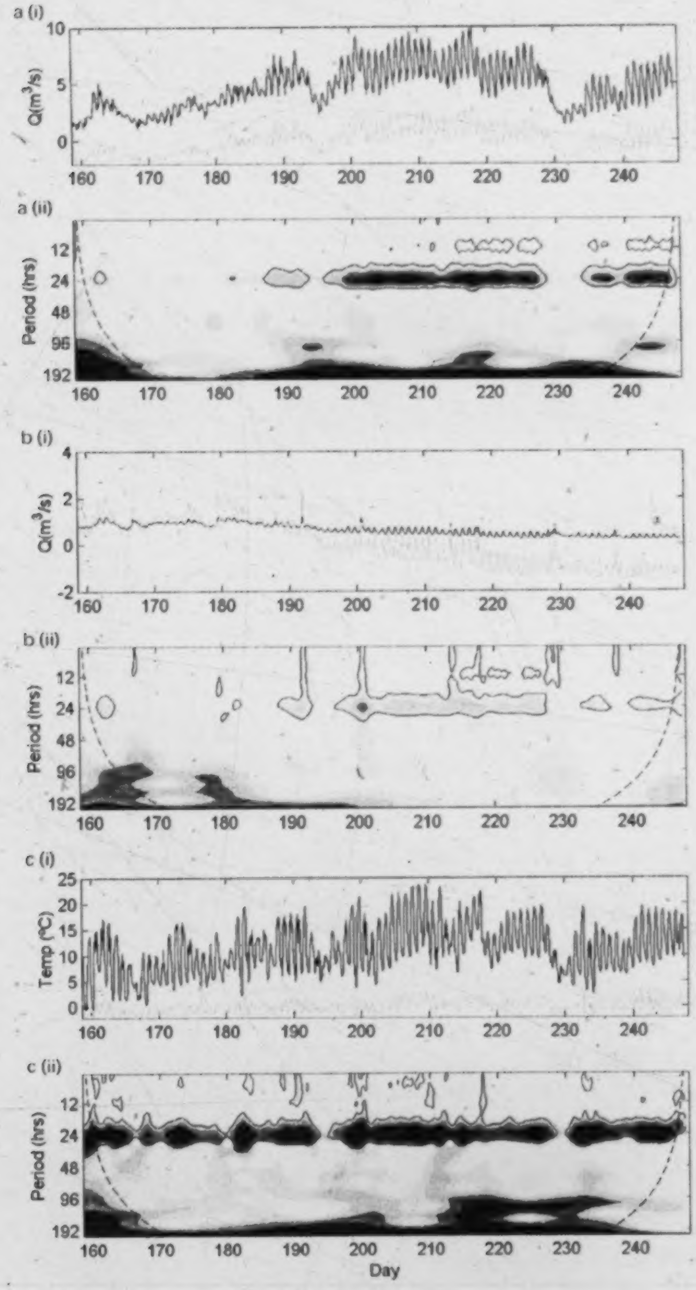

Figure 2.4 Time Series and Wavelet Spectra for 1998 (a) Q_{GL} (b) Q_{BR} (c) T. (i) The raw time series (black) and the mean centered and normalised time-series (gray). (ii) $W_n^{XX}(s)$ contoured at variance 0.5, 1, 2.5, 5, 10, and 20 (light to dark gray). The black line contours the areas where the power is considered significant, the dashed black line delineates the COI.

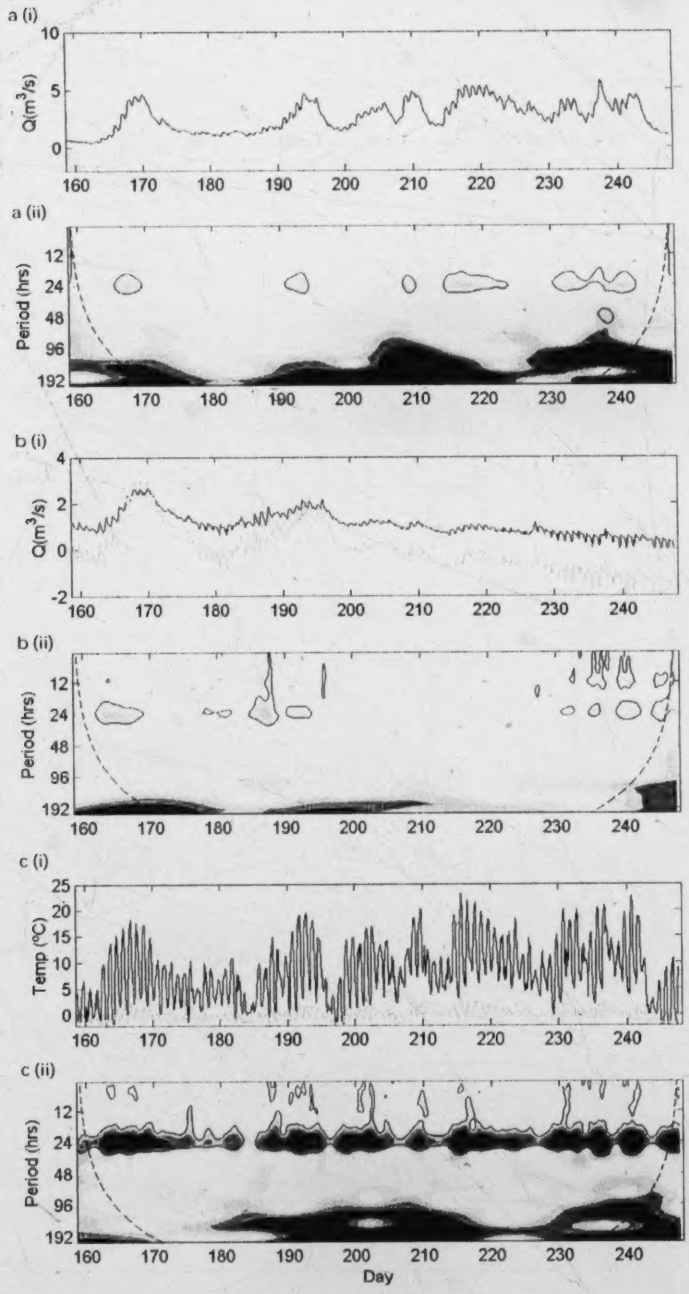

Figure 2.5 Time Series and Wavelet Spectra for 1999 (a) Q_{GL} (b) Q_{BR} (c) T. (i) The raw time series (black) and the mean centered and normalised time-series (gray). (ii) $W_n^{XX}(s)$ contoured at variance 0.5, 1, 2.5, 5, 10, and 20 (light to dark gray). The black line contours the areas where the power is considered significant, the dashed black line delineates the COI.

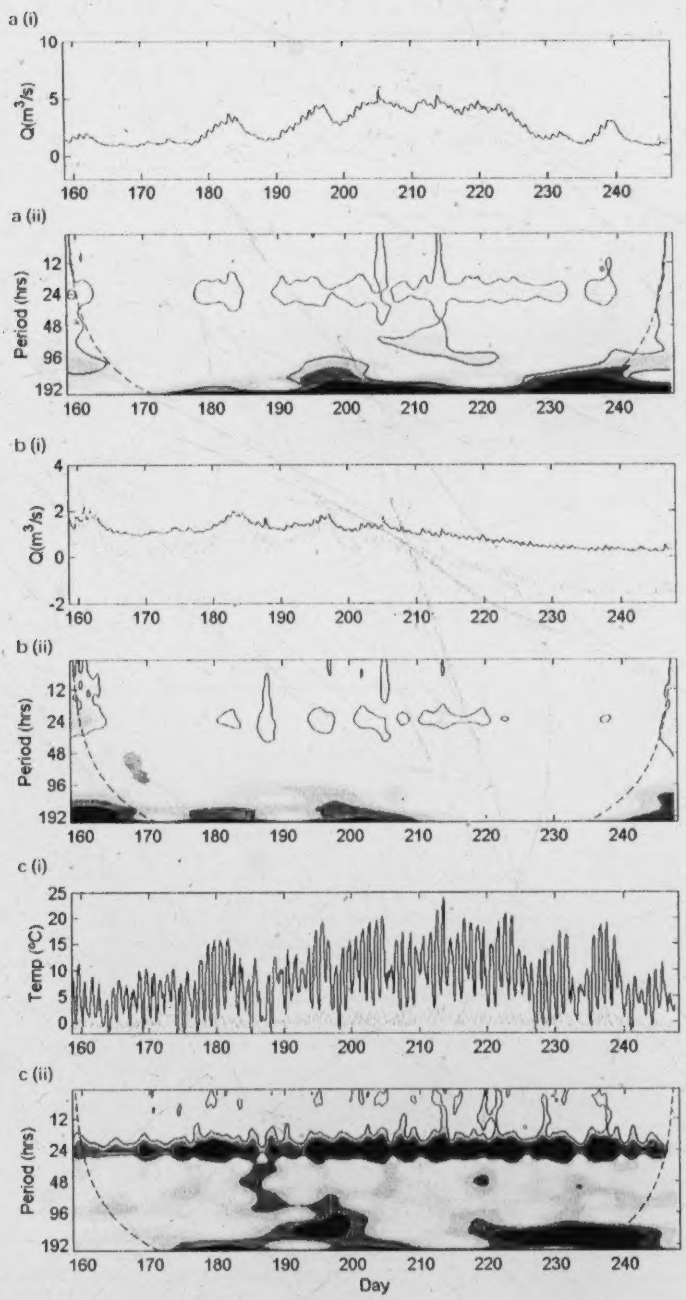

Figure 2.6 Time Series and Wavelet Spectra for 2000 (a) Q_{GL} (b) Q_{BR} (c) T. (i) The raw time series (black) and the mean centered and normalised time-series (gray). (ii) $W_n^{XX}(s)$ contoured at variance 0.5, 1, 2.5, 5, 10, and 20 (light to dark gray). The black line contours the areas where the power is considered significant, the dashed black line delineates the COI.

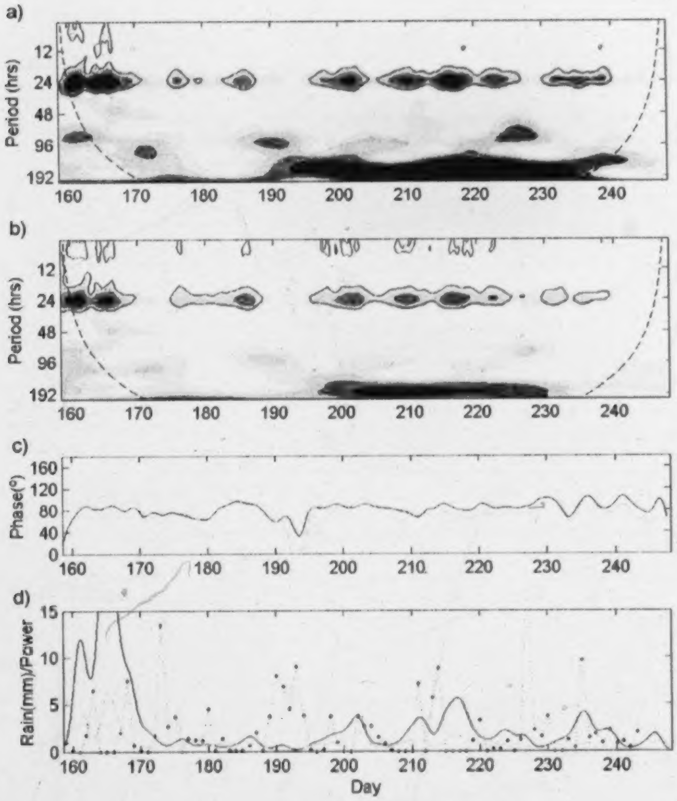

Figure 2.7 Cross wavelet analysis 1997 (a) Temperature and GL discharge cross-spectrum ($W_n^{TQ_{GL}}(s)$) (b) Temperature and BR cross-spectrum ($W_n^{TQ_{BR}}(s)$) with contours at variance 0.5, 1, 2.5, 5, 10, 20. The black contour is the 95% confidence level of the cross-spectrum, the dashed contour is the 95% confidence level of the discharge spectrum, and the dashed black line on the edges is the COI. (c) The phase difference at the 24 hour scale, $\theta_n^{TQ}(24)$, for GL (black), and BR (gray) (d) Power spectrum for Q at the 24 scale ($W_n^{QQ}(24)$) for GL (black) and BR (gray), and daily rainfall (dotted line with dots).

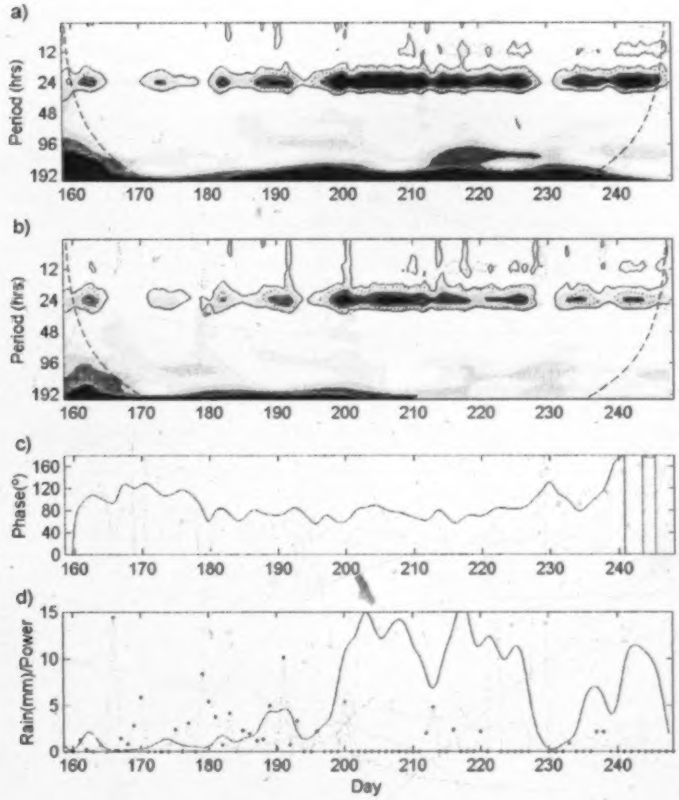

Figure 2.8 Cross wavelet analysis 1998 (a) $W_n^{TQ_{GL}}(s)$ (b) $W_n^{TQ_{BR}}(s)$ with contours at variance 0.5, 1, 2.5, 5, 10, 20. The black contour line is the 95% confidence level of the cross-spectrum, the dashed contour is the 95% confidence level of the discharge spectrum, and the dashed black line on the edges is the COI. (c) $\theta_n^{TQ}(24)$ for GL (black), and BR (gray) (d) $W_n^{QQ}(24)$ for GL (black) and BR (gray) and daily rainfall (dotted line with dots).

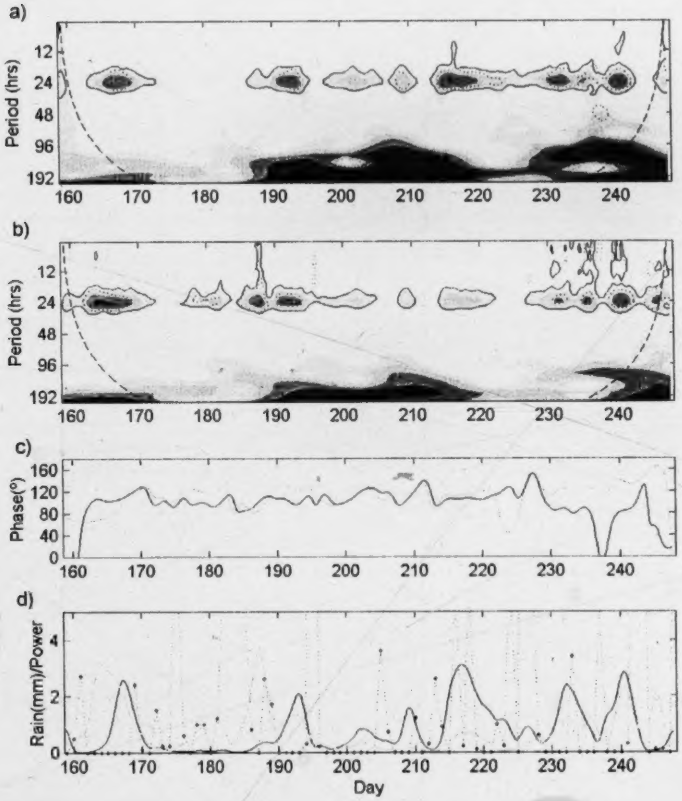

Figure 2.9 Cross wavelet analysis 1999 (a) $W_n^{TQ_{GL}}(s)$ (b) $W_n^{TQ_{BR}}(s)$ with contours at variance 0.5, 1, 2.5, 5, 10, 20. The black contour line is the 95% confidence level of the cross-spectrum, the dashed contour is the 95% confidence level of the discharge spectrum, and the dashed black line on the edges is the COI. (c) $\theta_n^{TQ}(24)$ for GL (black), and BR (gray) (d) $W_n^{QQ}(24)$ for GL (black) and BR (gray) and daily rainfall (dotted line with dots).

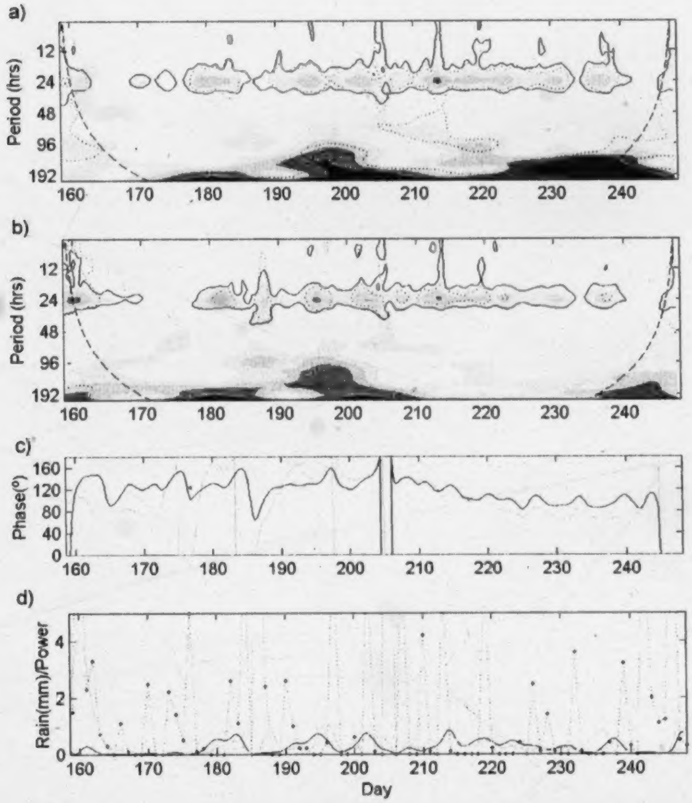

Figure 2.10 Cross wavelet analysis 2000 (a) $W_n^{TQ_{GL}}(s)$ (b) $W_n^{TQ_{BR}}(s)$ with contours at variance 0.5, 1, 2.5, 5, 10, 20. The black contour line is the 95% confidence level of the cross-spectrum, the dashed contour is the 95% confidence level of the discharge spectrum, and the dashed black line on the edges is the COI. (c) $\theta_n^{TQ}(24)$ for GL (black), and BR (gray) (d) $W_n^{QQ}(24)$ for GL (black) and BR (gray) and daily rainfall (dotted line with dots).

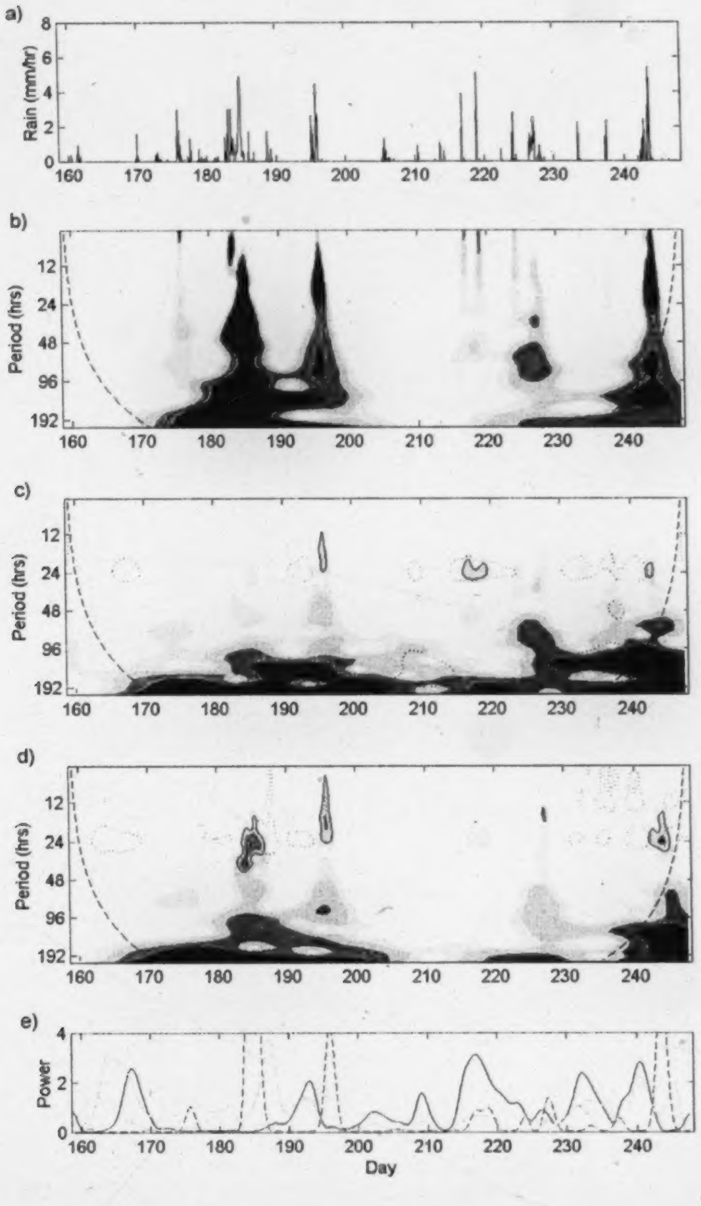

Figure 2.11 Wavelet analysis of hourly precipitation 1999 (a) Hourly rain (mm) (b) $W_n^{PP}(s)$ contoured at variance 0.25, 0.5, 1, 2, and 4 (light to dark gray) (c) $W_n^{PQ_{GL}}(s)$ (d) $W_n^{PQ_{BR}}(s)$, the cross-wavelet spectrums are contoured at powers of 0.25, 0.5, 1.0, and 4.0. The black contour line is the 95% confidence level of the cross-spectrum, the dashed contour is the 95% confidence level of the local discharge spectrum, and the dashed black line on the edges is the COI. (e) $W_n^{PP}(24)$ (dashed), $W_n^{QQ}(24)$ for GL (black) and $W_n^{QQ}(24)$ BR (gray).

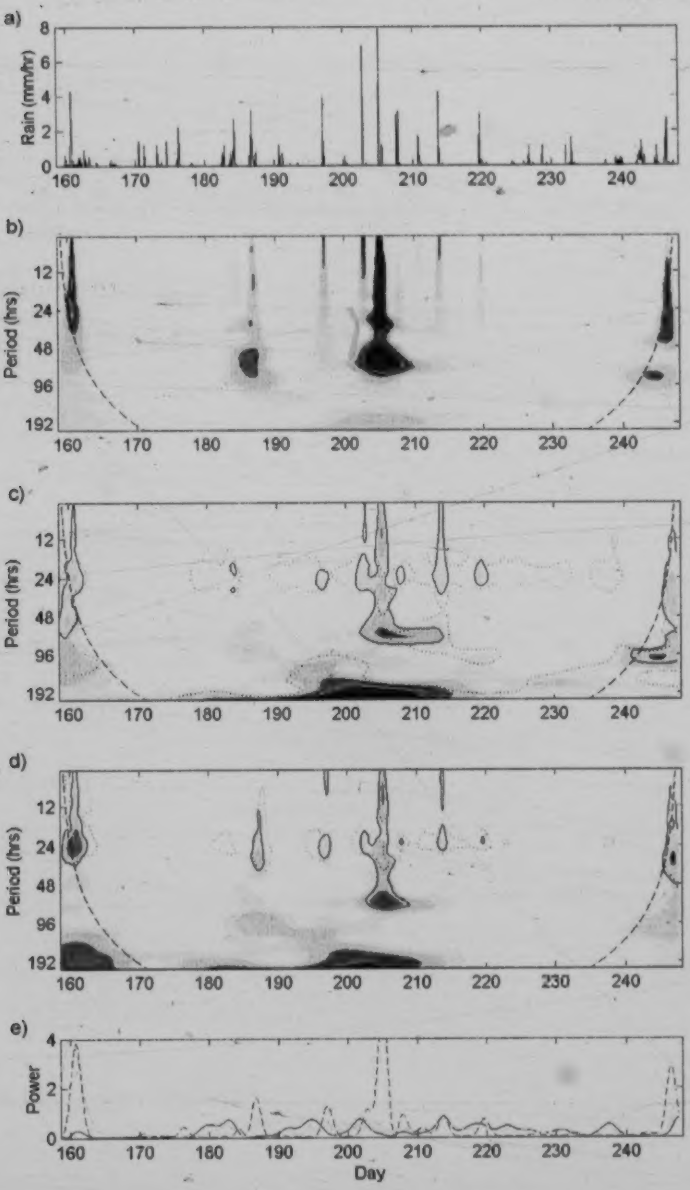

Figure 2.12 Wavelet analysis of hourly precipitation 2000 (a) Hourly rain (mm) (b) $W_n^{PP}(s)$ contoured at variance 0.25, 0.5, 1, 2, and 4 (light to dark gray) (c) $W_n^{PQ_{GL}}(s)$ (d) $W_n^{PQ_{BR}}(s)$, the cross-wavelet spectrums are contoured at powers of 0.25, 0.5, 1.0, and 4.0. The black contour line is the 95% confidence level of the cross-spectrum, the dashed contour is the 95% confidence level of the local discharge spectrum, and the dashed black line on the edges is the COI. (e) $W_n^{PP}(24)$ (dashed), $W_n^{QQ}(24)$ for GL (black) and $W_n^{QQ}(24)$ BR (gray).

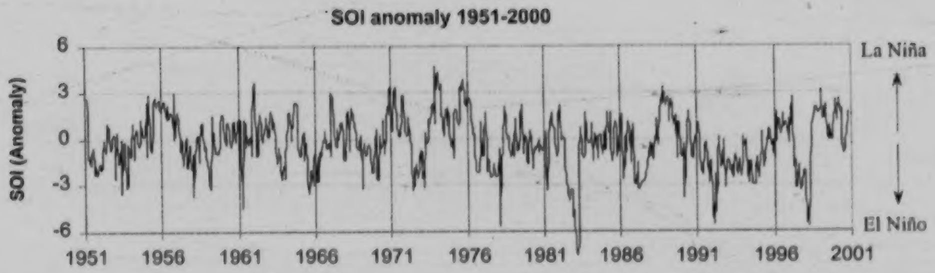

Figure 2.13 The Southern Oscillation Index (SOI) anomaly 1951-2000 (NOAA, 2000)

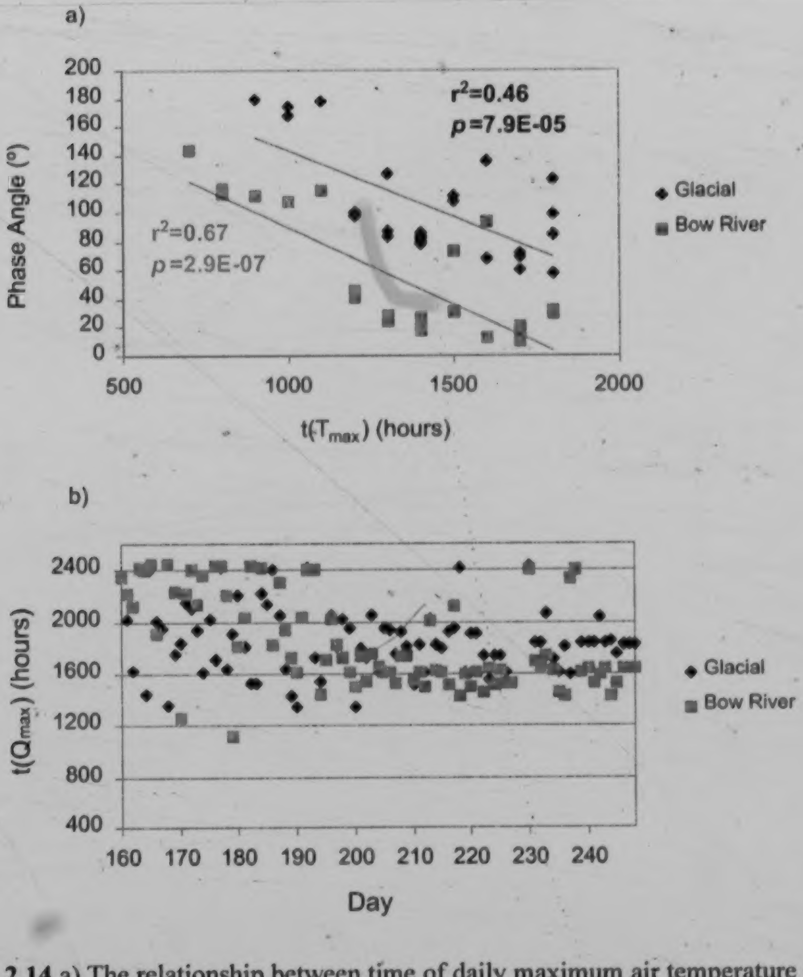

Figure 2.14 a) The relationship between time of daily maximum air temperature ($t(T_{max})$) and the phase difference ($\theta_n^{TQ}(24)$) at 12:00 for GLand BR between days 215-247, 1998. b) Time of daily maximum discharge ($t(Q_{max})$) for GL and BR 1998.

Chapter 3: Interpreting the flow routing of runoff and dissolved organic carbon sources in glacial and non-glacial catchments, using the concentration and spectrofluorometric properties of DOC [1]

3.1 INTRODUCTION

The chemical composition of surface waters reflects their hydrological pathway and their source. The concentration of dissolved organic carbon (DOC) and its spectrofluorometric properties have proven to be useful tools for investigating the flow routing of snowmelt, and the sources of DOC in runoff (Boyer et al., 1997; McKnight et al., 2001; Newson et al., 2001). In this study we examine the concentration and the fluorescence of DOC in the surface waters (snow melt, soil, and stream waters) of adjacent glacial and non-glacial catchments. Our goal is to investigate differences in the provenance (and abundance) of DOC in runoff from glacial and non-glacial environments and their implications for hydrological flow routing.

Snowmelt runoff may be routed through the soil profile or as overland flow (where the saturation or impermeability of soils limits infiltration, or where the snowpack is underlain by glacier). In alpine streams, DOC consists primarily of carbon that is leached from plant litter and soils by infiltrating snowmelt, and flushed to streams by shallow subsurface flow (Boyer et al., 1997; Hornberger et al., 1994). During a typical flushing event, stream DOC concentrations ([DOC]) increase dramatically at the onset of snowmelt, peak prior to maximum stream discharge, and then decrease to near pre-melt values by the end of the summer (Boyer et al., 1997; Hood et al., 2003; Hornberger et al., 1994; Lewis and Grant, 1979). Conversely, soil pore waters display a decrease in [DOC] during snowmelt, and begin to recover to higher values towards the end of the summer (Boyer et al., 1997), which is likely due to heterotrophic decomposition of soil organic matter as soil temperatures increase (Savage and Davidson, 2001).

On glaciers, snowmelt percolates downwards through snow and firn until it reaches the underlying ice surface. It then flows down slope until it either leaves the glacier surface or encounters a crevasse or moulin (Fountain and Walder, 1998). Most meltwater intercepted by crevasses and moulins drains via major englacial or subglacial conduits and has little interaction with subglacial sediments (Hubbard and Nienow, 1997). Some surface-derived runoff and meltwaters produced by basal melting may, however, drain by a more extensive distributed drainage system (consisting of thin water films, linked cavities and/or permeable subglacial sediments) that allows more significant water-sediment interaction. Waters routed through this component of the subglacial drainage system may make a significant contribution to runoff under recession flow conditions and early in the melt season before major drainage channels have developed. Although, subglacial environments can support bacterial populations, subglacial sediments typically contain very low amounts of organic carbon (Sharp et al., 1999; Skidmore et al., 2000). This is probably derived from glacially overridden soils, bedrock kerogen, or inwash from the glacier surface and valley walls (Margesin et al., 2002; Säwström et al., 2002; Sharp et al., 1999; Skidmore et al., 2000; Takeuchi, 2002). Although, we are not aware of any published reports of [DOC] in glacial runoff, we expect [DOC] to be relatively low, since most runoff probably has limited contact with organic matter.

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[1] A version of this chapter has been submitted for publication: Lafrenière, M. J. and Sharp M. J. The concentration and spectrofluorometric properties of Dissolved Organic Carbon in surface waters: interpreting the flow routing of runoff and DOC sources in glacial and non-glacial catchments, *Arctic, Antarctic, and Alpine Research*. (submitted December, 2002).

It is possible to qualitatively differentiate DOC that is derived primarily from terrestrial precursor material (from soil or plant organic matter) from DOC that is of microbial origin (products of algal and bacterial activity) using spectrofluorometric techniques (McKnight et al., 2001). The fluorescent properties of DOC vary with the aromatic carbon content of fulvic acids (Chin et al., 1994; McKnight et al., 2001). In rivers and alpine streams fulvic acids generally account for 30-70% of the DOC (Hood et al., 2003; Thurman, 1985). DOC derived from terrestrial sources contains fulvic acids from plant litter and soil organic matter, which are generally more aromatic (because of aromatic components such as lignin) than fulvic acids formed from the components of microbial cells and by-products of microbial activity (Chin et al., 1994; Harvey et al., 1983; McKnight et al., 1994; Thurman, 1985; Wagner and Wolf, 1999). The spectrofluorometric character of DOC can therefore help to determine the flow routing of runoff by indicating the likely source of the fulvic acid fraction of the DOC in different catchments. DOC in streams fed by snowmelt runoff from vegetated areas of both glacial and non-glacial catchments will likely be composed of fulvic acids derived primarily from plant litter and soil organic matter. Most fulvic acid from the surface of a glacier will likely be primarily the result of microbial activity in melt water (e.g. primary productivity of algae and bacteria in cryoconites or snow, Margesin et al., 2002; Takeuchi, 2002). Old plant-derived carbon may provide an energy source for microbial populations in subglacial soils and sediments (Welker et al., 2002), but its characteristics are likely changed considerably over time due to recycling within the microbial ecosystem. Indeed, microbial biomass may become an important component of the organic carbon reservoir within subglacial sediments (Wagner and Wolf, 1999; Wetzel, 1992). Thus, glacial runoff may contain DOC derived primarily from microbial activity (i.e. from the decomposition of microbial biomass, by-products of microbial metabolism, and/or primary productivity). To our knowledge, this is the first paper to examine the concentration and fluorescence of DOC in glacial runoff, and to compare the patterns of seasonal variation in these parameters in runoff from adjacent glacial and non-glacial catchments.

3.2 SITE DESCRIPTION AND INSTRUMENTATION

The study was conducted at Bow Lake, Banff National Park, Alberta, Canada (51°40N, 116°27W). Two main catchments feed Bow Lake; one is substantially glaciated, the other is virtually unglaciated (<1.5% ice cover) (Figure 3.1). The principal inflow to the lake is the Glacial stream (GL), fed primarily by meltwater from the Wapta Icefield. This catchment is approximately 27 km^2, with a mean elevation of 2560 m.a.s.l. 12% of the catchment is forested and overlain by soils with developed mineral horizons (brunisols and podsols) and some organic matter accumulation (Holland and Coen, 1982). The rest consists of glacier ice (41%, 11 km^2), till, and moraines on which soils are absent or poorly developed (i.e. regosols). The Glacial stream is a secondary stream with two tributaries, the Bow Hut (BH, 37% glaciated; 42% rock, till, and moraine; 21% forested) and the Bow Glacier (BG, 75% glaciated; 24% rock, till, and moraine; <1% forested). The source of the tributaries is the Wapta Icefield (Figure 3.1). From the snout of Bow Glacier, the BG stream falls approximately 100 m down a cliff into a proglacial lake, the outflow from the lake then falls another 120-150m, from here the stream flows over bedrock until it encounters till a short distance from the base of the cliff. The residence time of water in the proglacial lake is estimated to be 40 days. The BH stream originates in the valley southeast of Bow Glacier and flows over glacial till and bedrock. The GL stream also flows through glacial till. This stream was gauged and sampled approximately 800 m away from the canyon where the tributaries merge (Figure 3.1). The secondary non-glacial inflow, the Bow River (BR), flows through a subalpine meadow and drains into the north side of Bow Lake. This catchment has a mean elevation of 2310 m.a.s.l.. Its area is approximately 17 km^2, of which 67% consists of subalpine meadow and spruce-fir forests. The remaining area is sparsely vegetated (29%) or unvegetated (2%). The soils are primarily developed mineral soils with some organic horizons (63% of the catchment is overlain by brunisols, podsols and gleysols). Soils are absent or poorly developed in the rest of the catchment (Holland and Coen, 1982).

DOC samples were collected from the Glacial stream and the Bow River approximately every 3-7days during the spring and summers of 1998, 1999 and 2000 (the stream sampling locations are the same as the stream gauging stations, as shown in Figures 3.1 and 3.2). Occasionally, multiple samples (up to 5) were collected in a single day (between approximately 800h and 2100h) to monitor diurnal variability. In 1998 and 1999 the Bow Hut and Bow Glacier streams were also sampled every 3-7days. In 1999 and 2000 well water samples were collected from Numtijah Lodge (NT), located on the north side of Bow Lake (Figure 3.1). During the 2000 snowmelt period (April-July 2000), DOC samples were collected from the snow, snowmelt, and soil lysimeter sites (Figure 3.2).

The discharge of the Glacial and Bow River streams was also monitored during the summers of 1998, 1999 and 2000. Gauging stations on each stream recorded hourly and daily averages of 10-second measurements of stage using a Keller 169 pressure transducer and Campbell CR10 datalogger. The stage records were converted to discharge using rating curves based on discharge measurements made by the velocity area method. The error associated with the discharge measurements is estimated to be ±10% (Dingman, 1993).

Eight tension soil lysimeters were installed at four sites in August 1999. Sites were chosen in order to sample a range of soil types in the lake catchment that might have different flow regimes during snowmelt. There were two sites (S1 and S2) in each of the Glacial and Bow River catchments (Figure 3.2). Two lysimeters were installed at each site, one at 24 cm depth and one at 12 cm depth. Tension lysimeters consisted of a PVC tube fixed to a porous ceramic cup. The top of the tube was sealed with a rubber cap fitted with an extraction tube. Lysimeters were soaked overnight in deionised (DI) water and then rinsed in DI water prior to installation in the field. Each lysimeter was evacuated once prior to sampling in spring 2000. Samples were extracted using a hand held vacuum pump and HDPE tubing that was cleaned by rinsing with 30% hydrogen peroxide and DI water. To minimize contamination and disturbance of the surrounding snowpack, soil lysimeters were not sampled until the snowpack at each site was very thin (<25 cm).

Two snowmelt collectors were installed in October 1999 (Figure 3.2). One was installed in an area surrounded by mixed spruce/fir forest (Forest), the other was installed in the subalpine meadow, where nearby vegetation consists of grass, willows and sedges that are snow covered until late spring (Meadow). The collectors consisted of Plexiglas 'troughs' installed on a fixed base at a slight angle. These troughs collected meltwater that drained through an outlet directly into a covered plastic 10 L bucket. The wood base was sunk a few inches into the ground, and the bucket was housed in an insulated box in a hole below the ground surface. The troughs and plastic buckets were soaked and rinsed in DI water, then covered and sealed in clean plastic until field installation was complete. Snowmelt was sampled by carefully digging out the box and dispensing the contents of the bucket into sample bottles. Solid snow samples were collected from pits dug near the snowmelt collector.

3.3 SAMPLING AND ANALYTICAL METHODS

Stream, snowmelt, and soil water samples were filtered on-site using glass filtration apparatus and Whatman GF/F glass fibre filters. The filtrate was transferred to amber glass EPA vials, acidified to pH 2 with HCl, and refrigerated until analysis. Prior to sampling, vials were rinsed with DI water and combusted overnight at 550°C. The filtration apparatus was soaked and rinsed with 30% hydrogen peroxide, DI water, and sample between each use. Snow was collected by inserting clean wide mouth glass jars (rinsed in DI water and combusted overnight at 550°C) into the face of a snowpit. Snow samples were stored frozen, and melted, filtered and acidified just prior to analysis.

The concentration of DOC was measured as non-purgeable organic carbon (NPOC) by high temperature combustion (680°C) with a Shimadzu TOC 5000A analyser equipped with high a sensitivity platinum catalyst. The detection limit (Miller and Miller, 1988) for the analysis of snow and stream samples was 0.19 ppm, based on the analysis of sample blanks (DI water that was filtered, stored and analysed as field samples, n=6). Based on duplicate determinations of similar samples, the uncertainties in the precision of the measurements ($p<0.05$) were ±0.07 (n=7), ±0.02 (n=9) and ±0.03 ppm (n=5), for 1998, 1999, and 2000 samples, respectively (Kretz, 1985). Soil solution samples from the tension lysimeters were diluted to [DOC] < 3 ppm with DI water (1:5 or 1:10 dilutions) before DOC analysis. DOC concentrations reported for soil solutions were corrected for the concentration of DOC in DI water used in the dilution. The uncertainty for soil water DOC was ±0.21 ppm ($p<0.05$), based on duplicate determinations (n=13) (Kretz, 1985).

The fluorescence of the DOC was measured using a Shimadzu RF-1501 scanning spectrofluorometer with a xenon lamp. Samples were scanned in an optically clear quartz cuvette (path length = 1.000 cm). Scans were performed at an excitation wavelength of 370 nm, for emission wavelengths between 370 and 700 nm at 1 nm increments. Scans of sample blanks of

DI water were performed, and the blank fluorescence values were subtracted from the raw scans of the samples in order to remove the effects of Raman scattering (Donahue et al., 1998; McKnight et al., 2001; Wolfe et al., 2002). After subtracting the blank, the fluorescence index (FI -the ratio of emission intensity at 450 nm to 500 nm for an excitation of 370 nm), the peak intensity of fluorescence, and wavelength of peak fluorescence (λF_{max}) were determined. The FI has values of ~1.9-2.0 for predominantly microbial DOC, and values of ~1.4 for DOC with predominantly terrestrial sources (Donahue et al., 1998; McKnight et al., 2001; Newson et al., 2001). The λF_{max} also varies according to provenance, with microbial DOC peaking at lower wavelengths (~445 nm) than soil/vegetation derived DOC (~455 nm) (McKnight et al., 2001). Uncertainties for FI and λF_{max} were 0.03 and 4.7 nm ($p<0.05$, $n=24$), respectively, based on the analyses of duplicate samples (Kretz, 1985). McKnight et al. (2001) state that, in general, a difference of at least 0.1 in the FI may be indicative of a difference in source of fulvic acids.

The oxygen isotopes ($\delta^{18}O$) of water were measured on a VG MM 903 triple faraday cup collector mass spectrometer at the Environmental Isotope Laboratory (EIL) at the University of Waterloo, Ontario, Canada. The EIL uses the standard procedure for oxygen isotopes (Epstein and Mayeda, 1953). All $\delta^{18}O$ results are reported as per mille (‰) VSMOW. The uncertainty in the measurements is ±0.1‰ based on 11 duplicate analyses. Cation concentrations were determined by ion chromatography on a Dionex DX500 ion chromatograph equipped with a CRSR-Ultra self-regenerating suppressor, and CS-12A analytical and guard columns. The uncertainties in the ion concentrations ($\mu eq \cdot L^{-1}$) were estimated using analyses of 16 duplicate samples run on separate days (Kretz, 1985). The uncertainties were (SE $\mu eq \cdot L^{-1}$, CV% in brackets, $p<0.05$): Mg^{2+} ±19 (2%), Ca^{2+} ± 25 (2.0%).

3.4 RESULTS

3.4.1 Variability between sites

In the Bow River, [DOC] ranged from ~0.4 to 2.1 ppm, and the mean [DOC] was more than double that found in the other streams (Table 3.1). In the Glacial stream and its tributaries (BH and BG) [DOC] was always <1 ppm (Table 3.1). In 1999, the mean [DOC] for these three streams was similar to that in groundwater sampled at the lodge (NT). The mean [DOC] in snow was also similar to the mean [DOC] of the glacial streams. Snowmelt was, however, enriched in DOC relative to the snow samples. [DOC] in the soil lysimeter samples was 5 to 10 times higher than [DOC] in other surface waters (Table 3.1).

Table 3.2 lists the mean values for fluorescent properties (FIs and λF_{max}) and [DOC] for each sampling site. The Glacial stream, the groundwater, and the meadow snowmelt had the highest mean FIs (1.64-1.71), and lowest mean values for λF_{max} (~440-443 nm). The Bow River, the soil pore waters from both sites, and the snowmelt from the forest lysimeter defined the low end of the FI range (1.45-1.49), and the high end of the range for λF_{max} (~453-454 nm). In general, FI was inversely related to [DOC] (Figure 3.3a). The regression (a power function) defining the relationship is significant at $p<10^{-5}$, but weak ($R^2=0.25$). Thus, [DOC] does not account for a large proportion of the variability in FI. For example, even when [DOC] is similar in the Glacial stream and the Bow River, FI is usually higher in the Glacial stream samples than in the Bow River samples (Figure 3.3b). Also, [DOC] in the soil solutions are significantly higher than in the Bow River, but the FI values are similar (Table 3.2).

The statistical significance of the differences in [DOC], FI, and λF_{max} between and within the various sampling sites was evaluated using a one-way analysis of variance (ANOVA). For all variables, there was more between site variability (for the 2 streams, groundwater, the 2 soils lysimeters, and the 2 snow melts), than within site variability ($p<0.01$). Post-hoc analysis was performed to determine which sites were significantly different from each other. Duncan's multiple range test (StatSoft, 1997) revealed that the fluorescent properties of DOC (FI and λF_{max}) from the Bow River were significantly different from those of the Glacial stream, the groundwater and the meadow snowmelt (FI was significantly lower, and λF_{max} was significantly higher, $p<0.05$). The Glacial stream DOC was significantly different from that from the Bow River, soil waters and Forest snowmelt (FI was significantly higher, and λF_{max} was significantly lower). The fluorescence properties of Bow River DOC were therefore similar to those of the soils, while the fluorescence properties of the Glacial stream DOC were similar to those of DOC from the groundwater and Meadow snowmelt.

3.4.2 Seasonal and inter-annual variability of stream [DOC]

Except for very late in the summer, [DOC] was much higher in the Bow River than in the Glacial stream (Figure 3.4). In the Bow River, [DOC] showed a clear and consistent seasonal pattern every year, peaking at the start of the melt, prior to the peak in stream discharge (Figure 3.4). For this stream, linear regressions of [DOC] against time for the period between the seasonal maximum and minimum are virtually identical for 1999 and 2000 ($DOC_{1999} = -0.022*days + 5.10$, $r^2=0.94$, $p<0.001$; $DOC_{2000} = -0.023*days$

+ 5.21, $r^2=0.89$, $p<0.001$). The pattern in 1998 was somewhat different, probably because snowmelt began before our sampling that year due to a thin winter snowpack and warm spring temperatures (Lafreniere and Sharp, 2003).

The Glacial stream showed a small increase in [DOC] coincident with the initial increase in stream discharge, but the magnitude and timing of the seasonal changes in [DOC] were inconsistent and ill defined (Figure 3.4). The Glacial stream [DOC] always remained low in late summer despite the significant increase in runoff (Figure 3.4). It is, however, difficult to estimate the degree of uncertainty associated with the last statement, given the low number of samples collected in late summer. The [DOC] in the Bow Hut tributary (BH) was usually marginally higher than in the Glacial stream, while [DOC] in the Bow Glacier tributary (BG) was slightly lower than in the Glacial stream (Table 3.2). There is a strong relationship between the mean stream [DOC] and the abundance of developed soils in the catchment drained by the stream (Figure 3.5). This suggests that the mean [DOC] in a stream may be controlled by the availability of terrestrial carbon in its catchment, or by the fraction of the catchment that is overlain by developed soils (i.e. soils other than regosols).

3.4.3 [DOC] and fluorescence of DOC in streams

Although the Bow River has a much larger seasonal variation in [DOC] than the Glacial stream, the fluorescence of the DOC in the Glacial stream (as indicated by FI), is much more variable (both seasonally and diurnally) than that of DOC in the Bow River (Figures 3.6). In the Bow River, FI was highest in the winter (1.50-1.54). FI decreased slightly (1.44-1.48) as [DOC] rose at the start of snowmelt, and then remained essentially constant through the rest of the summer (Figure 3.6a). There was no significant diurnal variability in FI (1.46-1.45) despite relatively large changes in the [DOC] (1.75-1.59 ppm, Figure 3.7a).

In the Glacial stream, the initial increase in [DOC] (from 0.23 to 0.71 ppm) coincident with the early snowmelt discharge (between days 123-143) was associated with a decrease in FI (from 1.72 to 1.58, Figure 3.6b). The Glacial stream displays significant variability in DOC fluorescence over diurnal and 2-3 day timescales (Figure 3.6b). These variations in [DOC] and DOC fluorescence are examined in more detail and in conjunction with variations in discharge, Ca^{2+}, and $\delta^{18}O$ to try to understand their causes (Figure 3.7b, 3.8a-b). The decrease in FI (from

1.82 to 1.54) between days 153.50 (12:00 hrs) and 153.63 (15:00 hrs) was associated with decreases in both [DOC] and [Ca^{2+}], and an increase in discharge (Figure 3.7b). The decrease in FI at 15:00, however, preceded the decreases in [DOC] (from 0.48 to 0.41 ppm) and [Ca^{2+}] (from 1425 to 1333 μeq/L), which were not noticeable until the sample collected at 18:00 hrs (Figure 3.7b). There was no rain on day 153, so the increase in discharge could only have been due to snowmelt runoff. This indicates that the afternoon snowmelt waters diluted the more concentrated 'baseflow' water (as indicated by the decrease in [Ca^{2+}] and [DOC]), but also provided enough terrestrial DOC to shift the FI towards lower values (1.82 to1.54) despite decreasing the [DOC] (Figure 3.7b).

Another dramatic change in FI of the Glacial stream DOC occurred between days 201 and 207 of 2000 (July 19-25th, Figure 3.8a). During the first part of this period (between days 201 and 203, July 19-21), discharge and FI increased, while [DOC] and [Ca^{2+}] decreased (Figure 3.8a). This discharge increase was likely due to snowmelt at higher elevations in the catchment and/or on the glacier surface, since there was no significant rain or snow at low elevations during this period. The increase in FI from terrestrial (FI=1.49, day 201) to significantly more microbial values (FI=1.72, day 203) at this time was opposite to that seen on day 153 (May 18), when an increase in discharge also diluted [Ca^{2+}] and [DOC], but FI shifted towards more 'terrestrial' values (compare Figures 3.7b and 3.8a).

On day 207 (July 25), when discharge increased as a result of a rainstorm late in the day, there was a corresponding increase in [DOC] and [Ca^{2+}], but a decrease in FI of the DOC (Figure 3.8b). There was also a dramatic increase in the stream suspended sediment load (field observations). This event differed from the previous ones in that the increase in discharge was associated with a slight increase in [DOC] and a significant increase in [Ca^{2+}] rather than a dilution. This might suggest that the rain dissolved DOC from plant and soil organic carbon sources, and Ca^{2+} from fine sediments in the proglacial part of the catchment, and that the solutes, sediment and DOC were probably delivered to the stream via overland flow. However, the stream chemistry also shows that following the rain (between 17:00 and 21:00 hrs), there was an increase in the Mg^{2+}:Ca^{2+} ratio (from 0.56 at 17:00 to 0.67 at 21:00, Lafreniere, unpublished data). In addition, there was only a slight decrease in the $\delta^{18}O$ of stream runoff (from -20.8 at 17:00 to -20.5 at 21:00), even though the $\delta^{18}O$ composition of the rainwater collected at the weather station near the lake outflow (Figure 3.1) at 19:00 was much heavier (-13.4‰ VSMOW) than that of the stream runoff (mean = –20.7, SD±0.4 ‰, n=21).

3.4.4 DOC in snow and snowmelt

The means for [DOC] in snow and snowmelt samples at the Forest site were higher than for snow and snowmelt samples at the Meadow site (Table 3.1). Snowmelt was enriched in DOC relative to the snowpack at both sites (Figure 3.9 a, b). The enrichment was usually greatest in the first fraction of the melt, but a very high [DOC] was also recorded near the end of the melt season at the Forest site (Figure 3.9b). The fluorescent properties of snowmelt DOC were also very different at each site (Figure 3.9c). FIs of snowmelt at the Meadow site were extremely variable (1.43-2.06), and there was no apparent seasonal trend, or relationship with [DOC] (Figure 3.9c). The average FI and λF_{max} of the Meadow snowmelt suggest that DOC in snow at this site was primarily microbially derived (Table 3.2). In contrast, FIs of DOC from snowmelt at the Forest site were usually low (1.33-1.49) and relatively constant, with the exception of the last sample (day 154), when FI reached 1.87 (Figure 3.9c).

3.4.5 DOC of soil solutions

With the exception of site BR-S1 12cm, most of the soil waters had similar [DOC] (Table 3.1) and displayed the same seasonal trends (Figure 3.10a-b). This lysimeter was disturbed over the winter, re-installed in the spring of 2000, and then flushed once prior to sampling. The differences in the trend and concentrations of DOC observed at this site are, therefore, most likely due to this disturbance. Hence, the results from BR-S1 12cm are not included in the subsequent interpretation and analysis.

The soil solutions from BR-S2 had the highest [DOC], with minimum concentrations approximately twice those at other sites (Table 3.1). For all locations, the 12 cm lysimeter had higher mean [DOC] than the 24cm lysimeter at the same site (Table 3.1). The higher [DOC] in the shallow soil layers is expected, since [DOC] normally decreases with increasing depth in the soil (Thurman, 1985). At all sites, [DOC] in soil solutions were low in June (5-10 ppm), and higher in July (20-40 ppm). Only a limited number of soil solution samples were available for fluorescence analysis because sample volumes were small (<8 ml) and most of the sample was required for [DOC] measurements. FIs for soil water DOC were relatively low and constant at both sites in mid summer (Figure 3.10c). At lysimeter GL-S1 24, FI increased at the end of summer, coincident with the increase in [DOC] (Figure 3.10c). There was not enough sample to determine the fluorescence of the late summer samples from BR-S1 24 (Figure 3.10c).

3.5 DISCUSSION

There are significant differences in both the quantity and fluorescence of DOC exported by the Glacial stream and the snowmelt fed Bow River (Table 3.2). Compared to the Bow River, in which [DOC] can exceed 2.0 ppm in early spring, [DOC] in the Glacial Stream is low (0.2-0.8 ppm) and displays minimal seasonal variability (Figure 3.4). However, the fluorescence of the DOC in the Glacial stream (as indicated by FI), is much more variable (both seasonally and diurnally) than that of DOC in the Bow River (Figures 3.6). Values of λF_{max} for the DOC in the Bow River runoff (Table 3.2) were very similar to those found in Deer Creek in the Colorado Rocky Mountains (FI 1.40-1.48, λF_{max} 452-454 nm, McKnight et al., 2001). FI values for DOC from the Glacial stream were, on average, relatively low (Table 3.2) compared to those of microbially derived DOC from lakes in the Antarctic (FI 1.7-2.2). λF_{max} values for most of the Glacial stream DOC samples are, however, in the same range as values for DOC from water samples from Antarctic Lakes (λF_{max} 435-445 nm, McKnight et al., 2001) (Table 3.2).

The content and fluorescence of DOC in snow and snowmelt also vary significantly. It is likely that the higher [DOC] in the snowpack and snowmelt at the Forest site is a reflection of higher inputs of particulate organic carbon (POC) from surface litter and debris fall from the surrounding spruce/fir forest (McKnight et al., 1993; Thurman, 1985). The lower [DOC] in snow at the Meadow site can probably be explained by the fact that most of the vegetation (willows and sedges) is buried until near the end of snowmelt. Visual inspection of filter papers from snow DOC samples confirmed that there was substantially more particulate organic matter in snow from the Forest site. Although there was not enough material on the filters to quantify the inorganic and organic particulate fractions, the low pH of the snow (5.5-6.5) suggests that there was little inorganic (carbonate) particulate matter in the snow. The mean [DOC], FI and λF_{max} also indicate that in areas where there is significant exposed vegetation, the DOC in snowmelt is likely derived from leaching of terrestrial POC contained within the snowpack (Table 3.2). In contrast, where vegetation is absent or buried, snowmelt DOC appears to be derived predominantly from microbial activity in the snowpack (Table 3.2).

The large variations in the FI in the snowmelt suggest that where sources of terrestrial DOC are limited (as in the Meadow site) the make up of the fulvic acids can readily shift from terrestrial to microbially dominated (Figure 3.9c). This is conceivable if, for example, there is an input of a limited amount of plant derived organic matter. Initial snowmelt may leach DOC from this organic matter, resulting in DOC with a terrestrial FI. If this organic matter or DOC is subsequently used as a substrate for bacterial growth, this could lead to an increase in the production of biogenic fulvic acids. Without any new inputs of terrestrially derived carbon, the microbially produced DOC could become the dominant fraction of the DOC, leading to a change in the fluorescence of the DOC. However, if there were an input of new plant derived carbon (POC or DOC) during later stages of the melt, the fluorescence of the DOC would reflect this change in source, until/unless the products of microbial activity were significant enough to change the fluorescence characteristics of the DOC. However, it could also be that the FI is responding to changes in the balance of DOC from derived from plant matter and DOC derived from primary algal productivity in the snow.

Seasonal trends in [DOC] and DOC fluorescence in the Bow River indicate that stream DOC originates from soil and plant organic matter that is flushed to the stream by shallow subsurface flow. [DOC] in the Bow River shows a characteristic flushing response (Boyer et al., 1997) in all three years, reaching maximum values near the beginning of snowmelt, prior to the peak in stream discharge (Figure 3.4). The decrease in FI at the start of the 2000 season indicates that the pulse of DOC in the Bow River at the onset of snowmelt was derived from terrestrial sources (Figure 3.6a). The higher FI (~1.52-1.55) for Bow River DOC prior to the onset of snowmelt suggests that groundwater (FI ~1.65) was a significant source of runoff and DOC at this time. The consistency in the amplitude of, and rate of recession from, the spring peak in [DOC] suggests that the flow routing and source of DOC do not vary appreciably from year to year, despite significant differences in the annual snowpack and spring air temperatures (Lafrenière and Sharp, 2003). The spectrofluorometric character of DOC in the Bow River shows more variability than in subalpine Deer Creek, in the Colorado Rocky Mountains (McKnight et al., 2001).

The trend in [DOC] in the soil pore waters is also consistent with the flushing of DOC from soils during spring snowmelt (Boyer et al., 1997). The low [DOC] in June suggests that DOC is flushed from soils during spring snowmelt (Figure 3.10a). The FIs of soil waters in the GL-S1-24cm lysimeter indicate that, in the spring, DOC is derived primarily from leaching of plant litter and soil organic matter (Figure 3.10c). The increase in the FI of the soil water DOC in late summer is coincident with an increase in [DOC] (Figure 3.10c). The observed increase in DOC in July may be partly due to evaporative concentration of DOC in the soil solutions as soils dry out over the summer. Nevertheless, an increase in DOC over the summer is also consistent with a build up of DOC in the soil water due to increases in soil temperature and the microbial decomposition of soil organic matter (Moore and Dalva, 2001; Yano et al., 2000). An increase in microbial activity in the soil should result in the production of plant derived fulvic acids (with low FI). However, in the absence of new inputs of plant derived substrates from surface soil horizons, the increase in microbial biomass (and fulvic acids from the decomposition of microbial cells and by-products of microbial activity) during the dry summer months could potentially cause the observed shift in the FI to higher values (from 1.45 to 1.54).

In the Glacial stream, the shifts in FI towards terrestrial values during the first stages of snowmelt (day 139-143, Figure 3.6b) and diurnal snowmelt events (day 153, Figure 3.7b), indicate that snowmelt runoff generated in the lower reaches of the catchment flushes terrestrially derived DOC to the stream, similar to what is observed in the Bow River catchment during snowmelt. The FI of DOC in the Glacial stream is, however, high (1.58) relative to that of Bow River DOC, and the [DOC] is relatively low. This likely indicates that a much lower fraction of snowmelt runoff from the Glacial catchment has contact with soil and plant derived organic carbon than snowmelt runoff from the Bow River catchment. Only 12% of the Glacial catchment is covered in developed soils, compared to 63% in the Bow River catchment.

In the Glacial stream later in July (days 201-203), when snow has disappeared from the valley, the increase in baseflow due to snow (and maybe ice) melt from higher elevations leads to a dilution of [DOC] (from 0.41 to 0.18 ppm) and a shift towards more microbial FI values (from 1.49 to 1.72, Figure 3.8a). This indicates that melt water from snow (and/or ice) in glaciated areas contains lower concentrations of DOC than snowmelt from non-glaciated parts of the catchment, and that this DOC is derived primarily from microbial activity. This is consistent with the observation that the DOC in snow from the Meadow site (where there was little exposed vegetation) was on average less abundant and more microbial in character than DOC from snow at the Forest site (where there was a nearby source of plant debris). The microbial nature of DOC in the Glacial stream could be the result of microbial and algal activity in snow on the glacier surface (Margesin et al., 2002; Säwström et al., 2002; Takeuchi, 2002), or in subglacial environments (Sharp et al., 1999; Skidmore et al., 2000). The more microbial nature of the DOC in the Glacial stream may also be due to runoff contributions from the proglacial lake (Figure 3.1), which likely contains DOC produced from aquatic algae and bacteria. The recycling of a limited supply of terrestrially derived organic carbon over long periods of time by microbes in the subglacial environment (where organic residue is largely isolated from new inputs of terrestrially derived organic carbon) might also lead to a progressive change in the nature of DOC. The trend towards more microbial values of FI in glacial runoff could reflect evolution of the subglacial microbial community structure from one dominated by heterotrophs feeding on plant matter to one composed of a mixture of autotrophs and heterotrophs that utilise autotrophic biomass as a substrate for respiration (Wagner and Wolf, 1999). However, further examination of DOC from glacial systems in late summer is required in order to better constrain the range of concentrations and fluorescence of DOC from subglacial environments.

The response of stream DOC to the rainstorm on July 25th (day 207), 2000, shows that late season precipitation can flush terrestrial DOC to the Glacial stream. The increases in solute concentrations, DOC, and discharge initially suggest that the rain dissolved DOC from plant and soil organic carbon sources, and that the solutes, sediment and DOC were probably delivered to the stream via overland flow. However, the relatively constant $\delta^{18}O$ composition of the stream water indicates that the increase in discharge is not the result of overland runoff of rainfall. The lack of an increase in the $\delta^{18}O$ composition of the stream water, and the higher $Mg^{2+}:Ca^{2+}$ ratio suggest that the discharge increase resulted from flushing of pre-event waters from tills and/or soils in the proglacial part of the catchment. The quick response of stream chemistry and discharge to the precipitation event requires that the infiltrating event water displaced water that could reach the stream via relatively fast (i.e. shallow) flow paths. The availability of fine sediment, and leaf and plant debris on the surface of the proglacial area could explain the input of terrestrial DOC and the increase in the suspended sediment load. Alternatively, the high concentration of solutes and suspended sediment could have resulted from re-arrangement and flushing of the subglacial drainage system. However, it seems unlikely that the subglacial environment could be a source for the higher concentrations of terrestrially derived DOC. Thus, the rain must have infiltrated the surface and flushed pre-event waters, DOC, sediments and solutes from the shallow subsurface.

3.6 CONCLUSIONS

Trends in [DOC] and DOC fluorescence indicate that DOC in the Bow River is derived from soil and plant organic matter, and that this terrestrially derived DOC is flushed to the stream by shallow subsurface flow at the onset of snowmelt. Snowmelt in ice-free areas of the glacial catchment also appears to be routed through the shallow subsurface, but DOC concentrations are relatively low since snowmelt runoff from this catchment has limited contact with organic soils or litter. The fluorescence of DOC in the Glacial stream in summer (when most runoff originates from ice-covered areas), suggests that DOC from glaciated regions is more microbial in character than that derived from ice-free areas. Summer rain appears to have an effect similar to early season snowmelt runoff, in that it results in the flushing of organic carbon derived from plants and soils to the stream via shallow subsurface flow paths.

The FIs of DOC in environments where sources of terrestrially derived organic carbon are limited (e.g. snowmelt, summer soil water, glacial meltwater) suggest that, although the microbial community may initially be using plant or soil derived organic matter as a substrate, in the absence of further input of terrestrial organic material, the composition of the DOC can evolve to one that is dominated by organic carbon derived from the by-products of the growing microbial community (i.e. the products of decomposition of microbial biomass and/or the products of microbial metabolic activity). Further study of changes in DOC and DOC fluorescence under these conditions is, however, required in order to confirm these interpretations.

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Table 3.1 [DOC] sample statistics by site: Bow River (BR), Glacial (GL), Bow Glacial tributary (BG), Bow Hut tributary (BH), Numtijah Lodge well water (NT). Soil sites are identified by catchment (BR or GL), site (S1 or S2, as in Figure 3.2), and lysimeter depth (12 or 24 cm). All concentrations are in ppm.

1998	BR	GL	BH	BG
Mean	0.91	0.44	0.53	0.44
SD	0.36	0.14	0.45	0.18
N	11	10	9	13
Min	0.50	0.32	0.29	0.24
Max	1.63	0.71	1.09	0.95

1999	BR	GL	BH	BG	NT
Mean	1.18	0.36	0.37	0.23	0.34
SD	0.46	0.14	0.07	0.11	0.06
N	22	22	11	11	2
Min	0.36	0.15	0.26	0.14	0.30
Max	1.95	0.77	0.45	0.52	0.38

2000	BR	GL	BH	BG	NT	Meadow Snow	Meadow Melt	Forest Snow	Forest Melt
Mean	1.41	0.39			0.44	0.28	0.57	0.41	1.70
SD	0.37	0.12			0.07	0.12	0.42	0.18	1.54
N	24	29			6	6	7	6	6
Min	0.44	0.17			0.37	0.14	0.22	0.26	0.75
Max	2.12	0.71			0.56	0.46	1.38	0.68	4.69

2000	BR S1-12	BR S1-24	BR S2-12	BR S2-24	GL S1-12	GL S1-24	GL S2-12	GL S2-24
Mean	40.3	9.9	30.5	17.7	11.3	11.0	15.7	12.9
SD	22.5	7.9	7.9	9.9	8.6	8.2	10.8	9.9
N	8	11	7	9	9	9	5	6
Min	20.1	4.8	17.5	10.1	4.9	4.5	6.2	6.2
Max	83.5	23.4	39.0	31.6	24.9	24.1	32.2	25.8

Table 3.2 Statistics (means±SD) for fluorescence properties by site: Bow River (BR), Glacial (GL), Numtijah Lodge well water (NT), soils (BR S1-24cm, and GL S1-24cm), and snowmelt.

Site	N	[DOC] (ppm)	FI	λF_{max} (nm)
BR	16	1.25±0.59	1.47±0.03	453±3
GL	17	0.35±0.15	1.64±0.13	440±13
NT	6	0.44±0.08	1.66±0.02	443±8
BR S1 -24cm	6	5.17±0.36	1.49±0.01	453±2
GL S1 -24cm	7	10.67±8.95	1.48±0.04	454±2
Meadow Melt	6	0.43±0.25	1.71±0.22	431±14
Forest melt	6	1.70±1.54	1.45±0.21	454±6.2

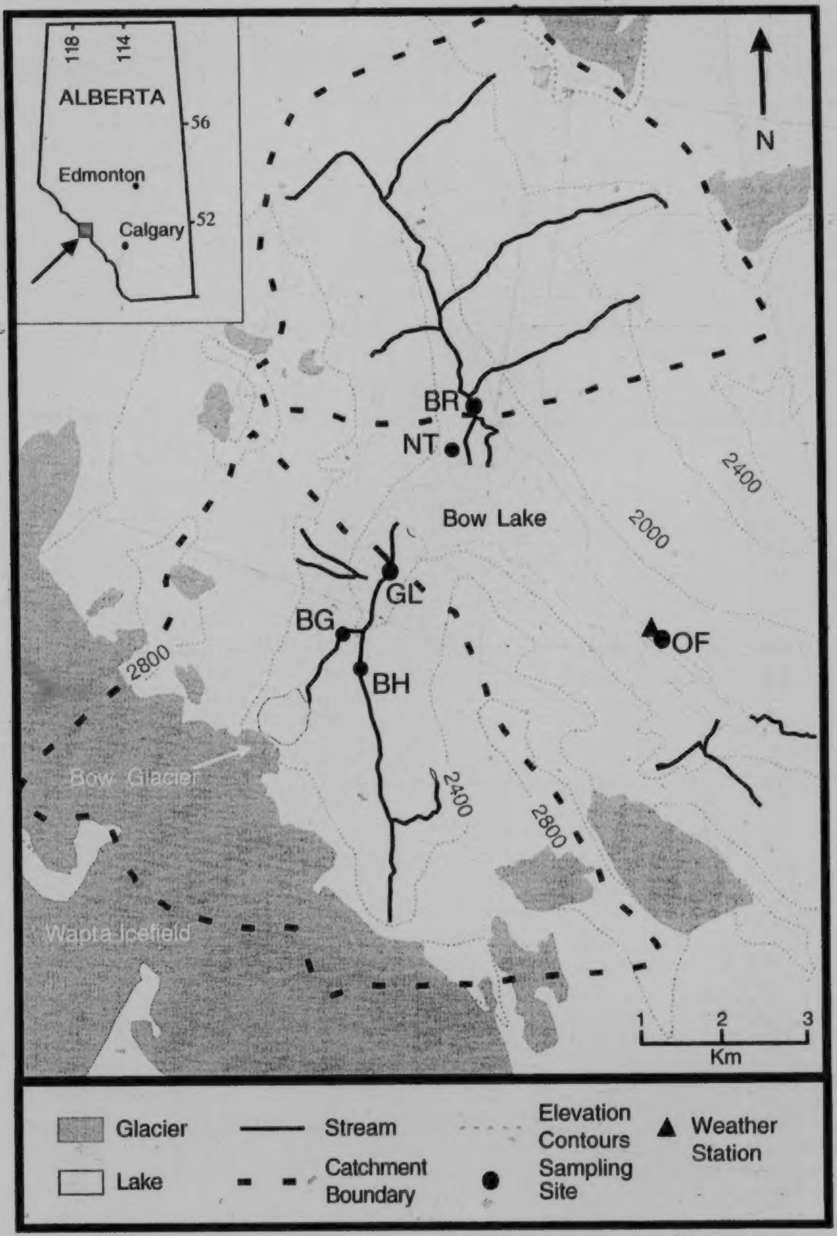
118
114
ALBERTA
56
Edmonton
52
Calgary
N
BR
NT
Bow Lake
2400
2000
GL
BG
BH
OF
2800
Bow Glacier
2400
2800
Wapta Icefield
1
2
3
Km
Glacier
Lake
Stream
Catchment Boundary
Elevation Contours
Sampling Site
Weather Station

Figure 3.1 Map of Bow Lake, illustrating the stream sampling (and gauging) locations for the Glacial stream (GL), the Bow River (BR), the Bow Glacier tributary (BG), the Bow Hut tributary (BH), Numtijah Lodge well water (NT), and the lake outflow (OF).

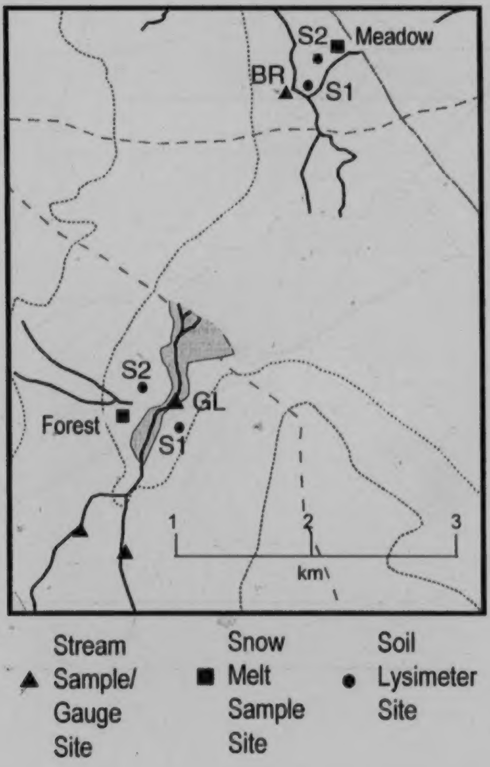
S2
Meadow
BR
S1
S2
GL
Forest
S1
1
2
3
km
▲ Stream Sample/ Gauge Site
■ Snow Melt Sample Site
● Soil Lysimeter Site

Figure 3.2 Map illustrating the location of stream, snow, and soil lysimeter sampling sites.

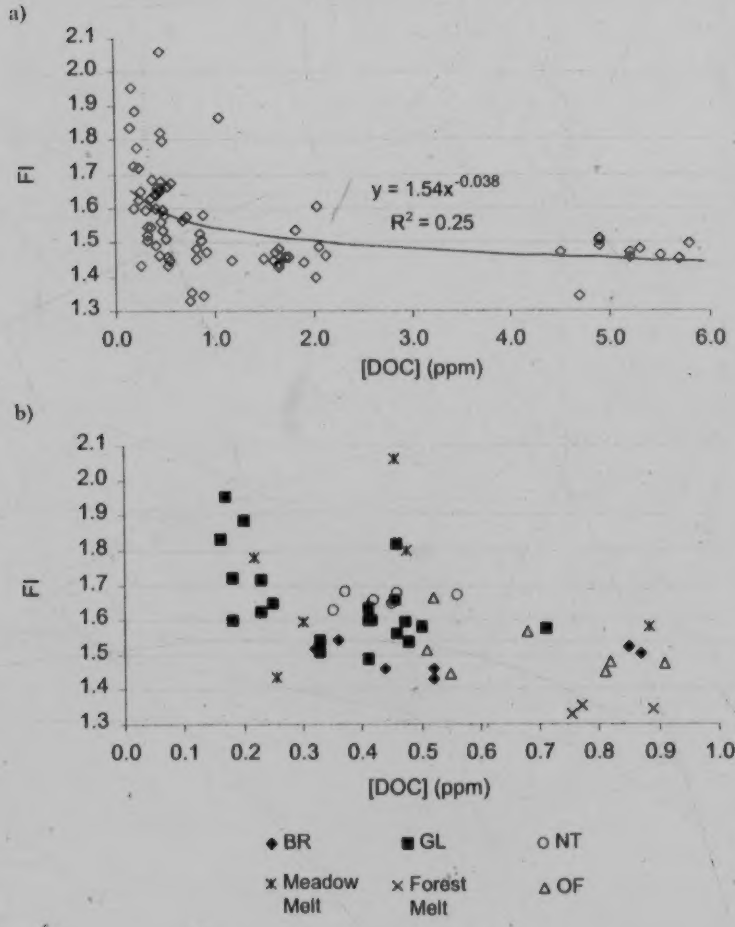

Figure 3.3 (a) FI vs. [DOC] for all samples grouped together. The 2 soil solutions with DOC >20 ppm are not shown on the graph, but they were included in the derivation of the regression shown ($FI=a*[DOC]^{b}$). (b) FI vs. [DOC] by sample site (excluding soils).

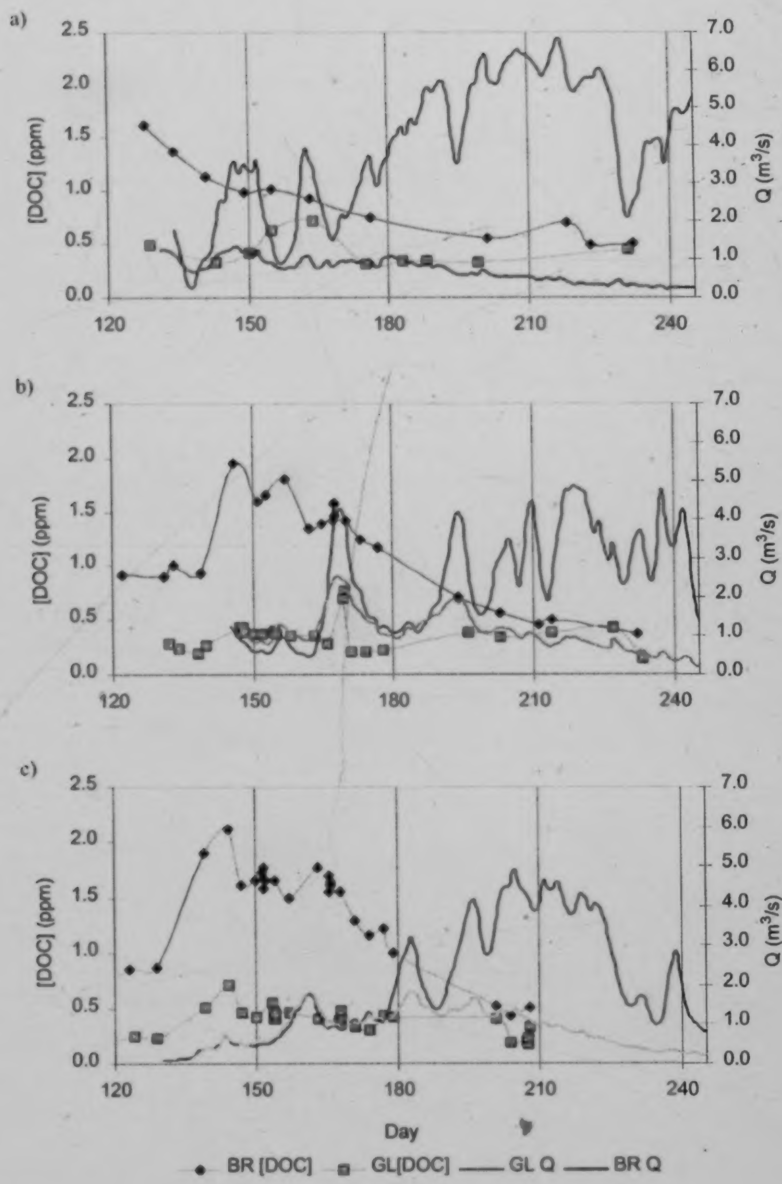

Figure 3.4 Stream [DOC] and discharge (Q) in the Bow River and Glacial stream May-August (a) 1998, (b) 1999, and (c) 2000.

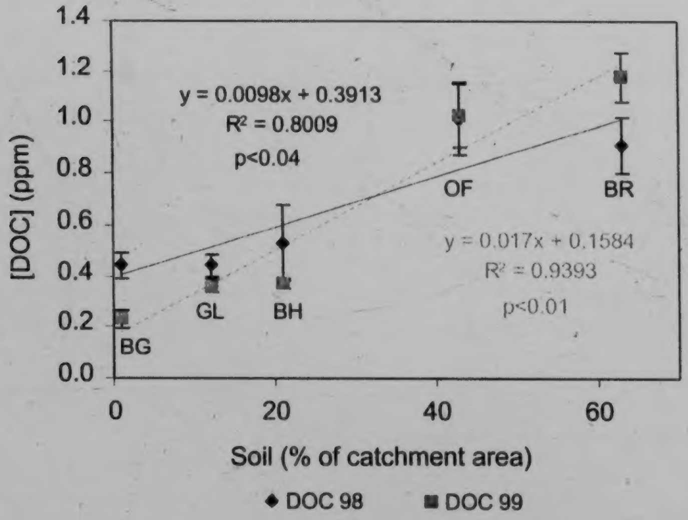

Figure 3.5 Relationship between mean [DOC] in stream waters (1998 and 1999) and soil covered area each catchment. Error bars are the standard error of the means. The regression equations, correlation coefficients (R^2), and level of significance (p) are indicated

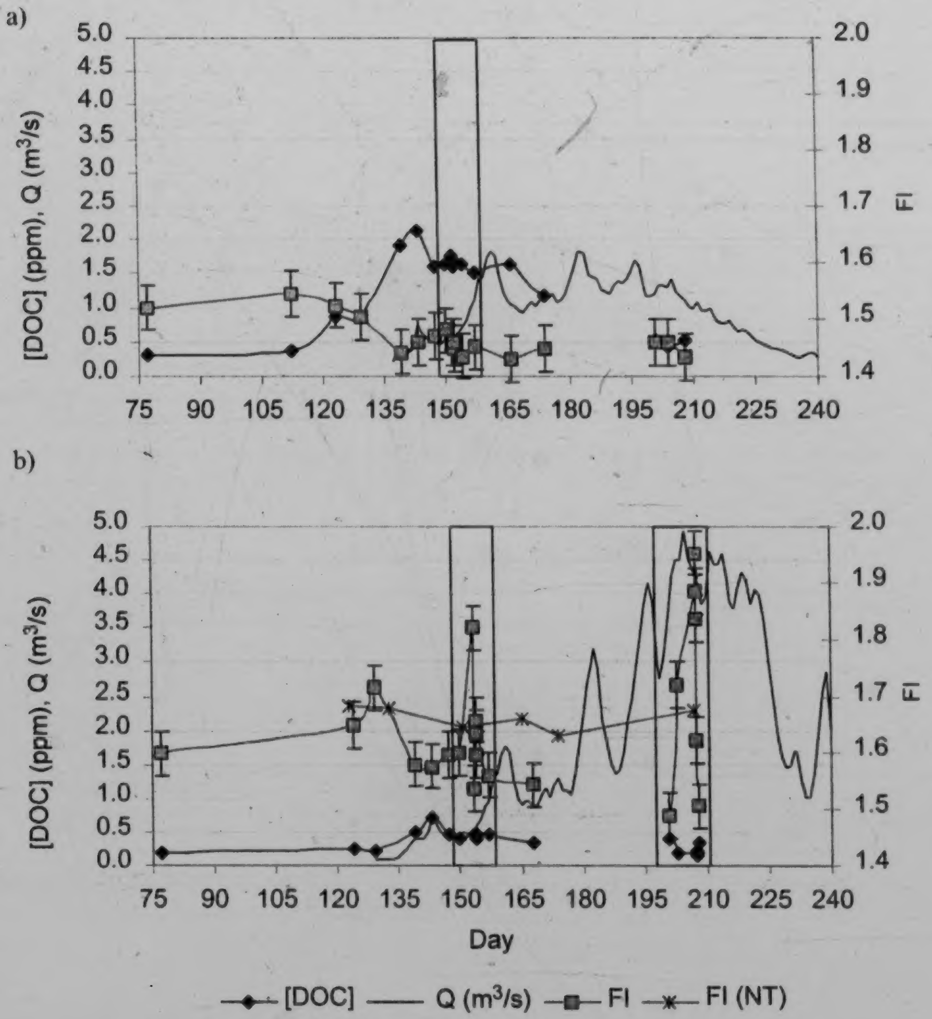

Figure 3.6 Seasonal trends in [DOC], discharge (Q m^3/s) and FI in 2000 for (a) the Bow River and (b) the Glacial stream. The FI for groundwater (NT) is also included in (b). Error bars are the uncertainty (±0.03) in the measurement of the FI as shown in Table 2. The boxed areas indicate the time series highlighted in Figures 3.7 and 3.9.

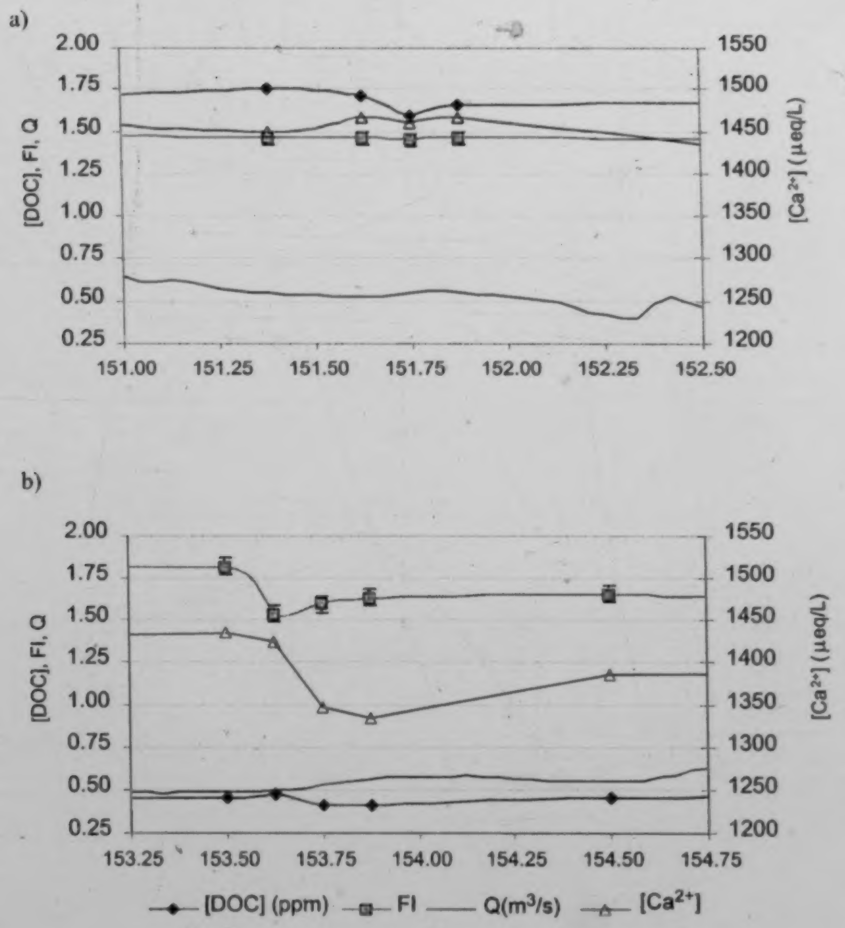

Figure 3.7 Diurnal variations in [DOC], FI, [Ca^{2+}], and discharge (Q m^3/s) in 2000 for (a) the Bow River (days 151-152) and (b) the Glacial stream (days 153-154).

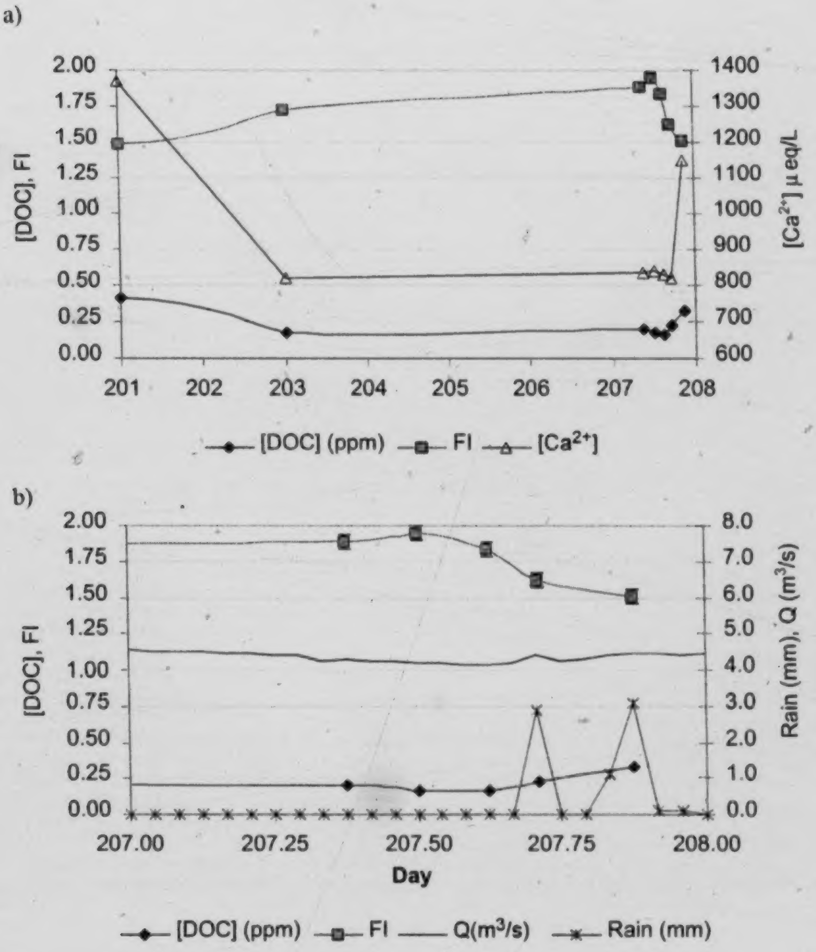

Figure 3.8 DOC in the Glacial stream, 2000. (a) [DOC], FI and [Ca2+] between days 201-208 (July 19-26) (b) Diurnal variations in [DOC], FI, rain (mm) and discharge (Q m3/s) on day 207 (July 25)

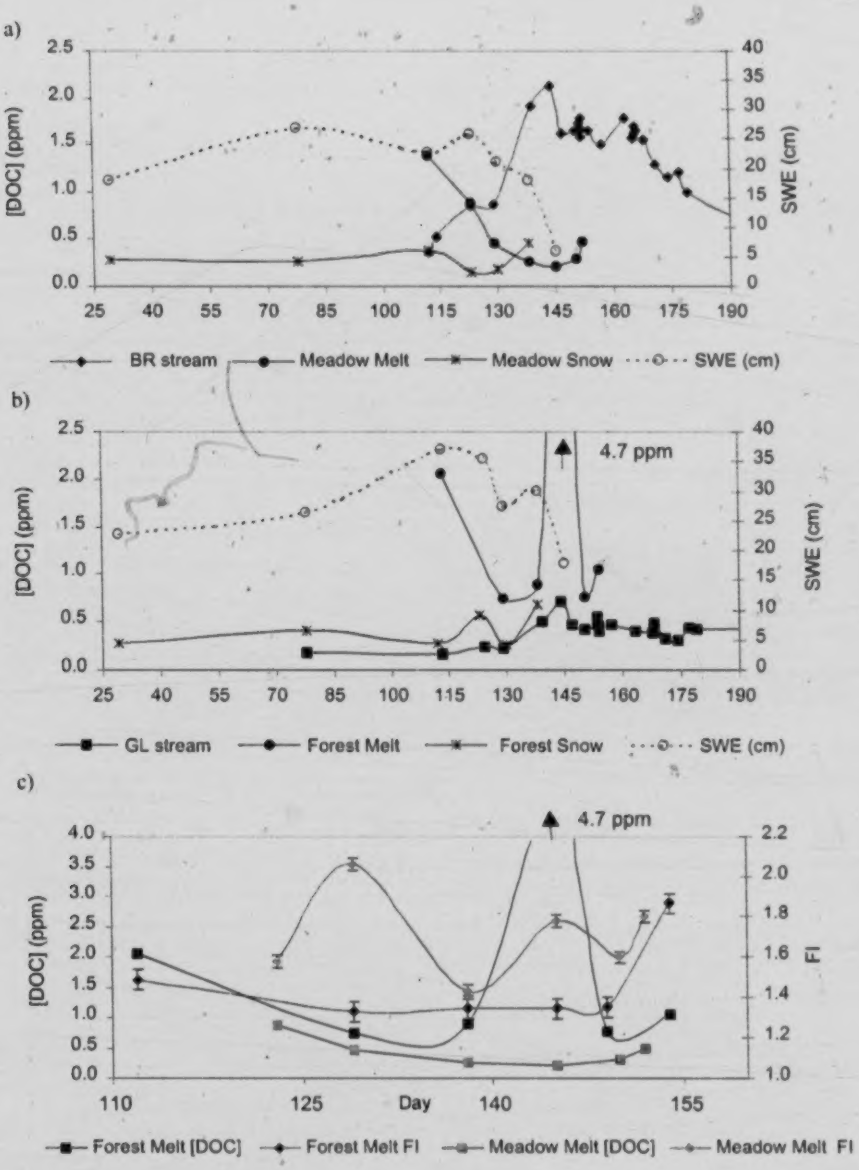

Figure 3.9 February-June 2000 (a) [DOC] for the Meadow snow, snowmelt, and stream [DOC] for the Bow River, with snow depth in SWE (cm); (b) [DOC] for the Forest snow, snowmelt, and stream [DOC] for the Glacial stream, with snow depth in SWE (cm); (c) Seasonal trends in [DOC] and FI for snowmelt.

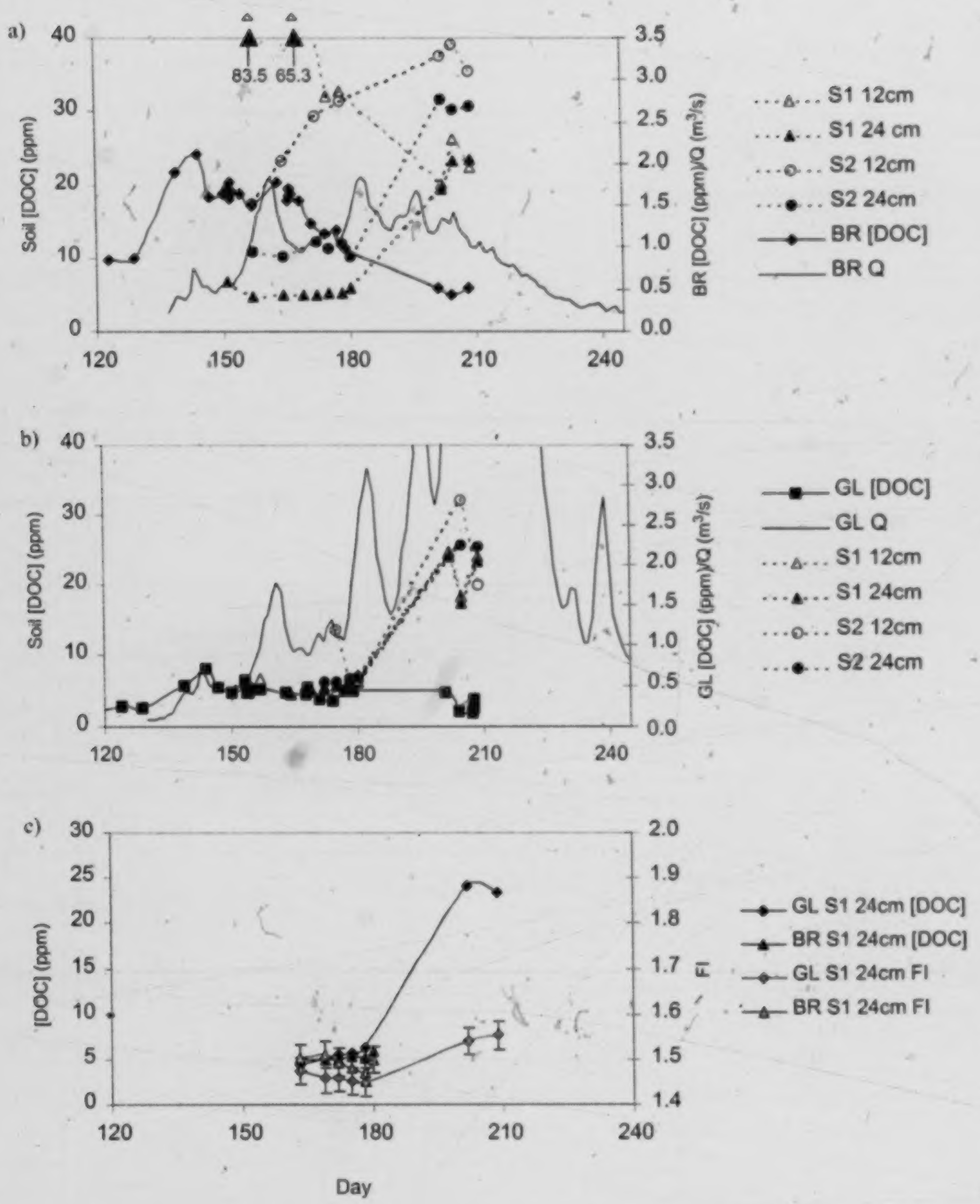

Figure 3.10 Soil water [DOC] and discharge (Q m^3/s) for (a) Bow River and (b) Glacial catchments (c) Soil water [DOC] and fluorescence index (FI)

Chapter 4: A comparison of solutes fluxes and sources from glacial and non-glacial catchments over contrasting melt seasons[1]

4.1 INTRODUCTION

This paper compares the fluxes of solute into Bow Lake in the Canadian Rocky Mountains from two streams, one glacial and one non-glacial, over three melt seasons: 1998, 1999, and 2000. The monitoring period included the strong 1998 El Niño event, and two relatively strong La Niña years (1999 and 2000) (NOAA, 2000). These events resulted in significant inter-annual variations in runoff from the two catchments (Lafrenière and Sharp, 2003), although the discharge responses to the climatic forcing were opposite in the two catchments. The lower snowfall and higher mean air temperatures in 1997-1998 resulted in higher runoff from the glacial catchment, and lower runoff from the snowmelt-fed catchment. Detailed analyses of runoff from the glacial catchment indicate that glacier ice was widely exposed in 1998 and that major subglacial channels likely developed during that summer. In contrast, ice exposure and subglacial drainage development were limited in 1999 and 2000 (Lafrenière and Sharp, 2003). In both the glacial and snowmelt fed streams, runoff responded more rapidly to air temperature changes in 1998 than in 1999/2000, indicating that the flow routing of melt water was faster/more efficient (Lafrenière and Sharp, 2003). This study examines how the solute fluxes and the composition of the solute load in the two streams responded to the inferred changes in runoff sources, runoff volumes and flow routing. The aim is to determine how the inorganic solute chemistry of runoff responds to seasonal and inter-annual changes in flow routing and runoff volume, and to differences in physical catchment properties (e.g. vegetation cover, ice cover).

Solute flux is the product of solute concentration and discharge. The dominant control on the solute composition of most small streams is rock weathering (Drever, 1997; Meybeck, 1987). Field and laboratory studies of mineral weathering indicate that the primary controls on weathering rates are: lithology (i.e. types of rock and minerals presents), the availability of protons (from snowpack, soils, carbonation or oxidation reactions), water:rock contact time, and the ratio between water volume and surface area of material available for weathering (Bluth and Kump, 1994; Brown et al., 1996; Fairchild et al., 1999b; Tranter et al., 1993; Tranter et al.,

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2002a). The principal distinctions between weathering in glacial and non-glacial environments are the presence of soils and vegetation in non-glaciated terrain, and the abundance of finely ground rock flour in glacial runoff and proglacial environments (Brown et al., 1994a; Brown et al., 1996; Fairchild et al., 1999a; Fairchild et al., 1999b). Glaciers can enhance physical and chemical weathering by exposing fresh reactive surfaces (high surface area/volume ratio, and strained mineral structure) to chemical attack (Brown et al., 1994a), while organic soils in non-glacial areas can accelerate weathering by supplying protons (carbonic acid, organic acids), which contribute to dissolution reactions. Reactions such as adsorption (of metals, and organics), and nutrient cycling also alter runoff chemistry from catchments where soils are present (Drever, 1997).

The primary controls on stream discharge are climatic, specifically precipitation and air temperature. In snowmelt-fed catchments total runoff is primarily dependent on the amount of snow accumulated over the preceding winter, and to a lesser extent on summer precipitation. In glacial catchments, inter-annual variability in runoff regimes results from variations in winter snowfall (which determines accumulation) and summer meteorological conditions. Summer meteorological conditions determine the extent of ablation and melting conditions on sub-annual timescales, which is true of snowmelt catchments as well. In unglaciated areas the hydrologic pathway may be as overland flow or as flow through the soil profile. In general, snowmelt as overland flow will tend to dilute runoff solute concentrations, while snowmelt that flows through the soil profile may lead to increases in the concentration of certain solutes (Lewis and Grant, 1979). Changes in annual snow depth and melt rates can affect flow routing (Hardy et al., 2001), and the extent to which the chemical composition of runoff is influenced by biogeochemical processes in soils (Brooks et al., 1995; Fitzhugh et al., 2001). In a glacial catchment snow and ice melt also dilute the baseflow solute concentrations. Ice melt is often more dilute than snowmelt because melting snow is leached of solutes prior to firnification and solutes are excluded from the crystal lattice as ice crystallizes (Fountain, 1996). Inter-annual variations in meltwater flux may be associated with variations in the degree of subglacial drainage system development, and thus in flow routing and water:rock contact times. These variations likely alter the balance of weathering reactions that yield solute to glacial meltwaters. They control the extent to which waters have access to chemically reactive rock flour, atmospheric carbon dioxide (Brown et al., 1994b), and environments in which microbially mediated reactions take place (Tranter et al., 1994; Tranter et al., 2002b).

4.2 SITE DESCRIPTION

Bow Lake is located in Banff National Park, Alberta, Canada (51°40N, 116°27W). The catchment is the source of the Bow River, which flows east from the Canadian Rocky Mountains into the interior plains of western Canada. Two main catchments feed Bow Lake; one is largely glaciated, the other is virtually unglaciated (<1.5% ice cover, Figure 4.1). The principal inflow to the lake is the Glacial stream (GL), fed primarily by meltwater from the Wapta Icefield. The glacial catchment is approximately 27 km^2 (as measured from the point of gauging, 3 km away from and approximately 400m below the snout of Bow Glacier) with a mean elevation of 2560 m.a.s.l. The catchment consists primarily of glacier ice (41%, 11 km^2), till, and moraines on which soils are absent or poorly developed (till, moraine & rock ~40%). Only 12% of the glacial catchment area is forested and/or overlain by soils with developed mineral horizons (brunisols and podsols) and some organic matter accumulation (Holland and Coen, 1982). The non-glacial inflow to the lake is the Bow River (BR). This catchment has a mean elevation of 2310 m.a.s.l. and is approximately 17 km^2. 67% of the catchment area consists of subalpine meadow and spruce-fir forests. The remaining area is sparsely vegetated (29%) or unvegetated (2%).

The geology of the Bow Lake catchment consists of Upper and Middle Cambrian carbonates and Lower Cambrian and Upper Proterozoic clastics (Price and Mountjoy, 1978). The Miette Group is within the Upper Proterozoic Windermere Supergroup (Hein and McMechan, 1994). In the Bow Lake area the Miette consists predominantly of slate and siltstone, feldspathic quartz sandstone and pebble conglomerates, as well as limestone and sandy limestone conglomerates (Price and Mountjoy, 1978). The Lower Cambrian Gog Group is mainly quartzite and quartzose sandstone (Price and Mountjoy, 1978), but in this area it likely contains the carbonate Peyto Formation, which is a unit of varied limestone, with some dolomite, sandstone and shale (Aitken, 1997). The Upper and Middle Cambrian carbonates include numerous limestone, dolomite and shale formations (Aitken, 1997; Price and Mountjoy, 1978). The Glacial stream catchment consists entirely of Upper and Middle Cambrian carbonates (Figure 4.1). The Bow River catchment contains all three groups, with the Miette Group in the valley floor (41% of the catchment area), the Gog Group on either side of the valley (42%), and the Upper and Middle Cambrian carbonates (17%) occupying higher elevations and steep slopes (Figure 4.1).

4.3 METHODS

4.3.1 Sample collection and analysis

Samples were collected from the Bow River and Glacial streams approximately every 3-5 days throughout the melt seasons of 1998, 1999 and 2000. Occasionally, multiple samples (up to 5) were collected in a single day (between approximately 800h and 2100h) to monitor diurnal variability. Samples were filtered on site through 0.45μm cellulose nitrate membranes immediately after collection. Two 20 ml aliquots of sample were collected in polyethylene scintillation vials, pre-rinsed with filtered sample, for anion and cation analysis. Alkalinity and pH were measured on site immediately following filtration. pH was measured using an Orion 290 digital meter, with automatic temperature compensation. The error on pH measurements is approximately ±0.1-pH units. Alkalinity (as HCO_3^-) was determined colorimetrically by titration with sulphuric acid, using a Hach digital titrator and brom-cresol green-methyl red indicator.

Ion concentrations were determined by liquid ion chromatography on a Dionex DX500 ion chromatograph. The uncertainty in ion concentrations was estimated from analyses of duplicate samples run on separate days (Kretz, 1985). The uncertainties based on 16 duplicates were (SE μeq/L, CV% in bracket), $p<0.05$): $Na^+ \pm 0.5$ (3%), $K^+ \pm 0.4$ (7%), $Mg^{2+} \pm 19$ (2%), $Ca^{2+} \pm 25$ (2.0%), $Sr^{2+} \pm 0.7$ (10%), $Cl^- \pm 0.3$ (4.0%), $NO_3^- \pm 0.5$ (10%) and $SO_4^{2-} \pm 4.9$ (1%).

The charge balance errors (CBE) were calculated as:

$$CBE = (\Sigma^+ - \Sigma^-)/(\Sigma^+ + \Sigma^-)\cdot 100 \qquad (1)$$

Where Σ^+ is the sum of cations, and Σ^- is the sum of anions. The mean CBE for stream meltwater was +6%, and the CBE for the majority of the samples was between 0-10%. The total errors on the results from ion chromatography were relatively small, and the charge associated with organic acids (DOC) in these waters is also a very small fraction (2-10%) of the charge imbalance (Cronan and Aitken, 1985; McKnight et al., 1985). Therefore, the most likely cause of the consistently positive charge balance is thought to be a systematic error in the colorimetric alkalinity titration. Where samples produced large charge balance errors (>10% or less than 0%), it was evident, from the concentrations and ratios of the other major ions, that there was a large error in the alkalinity measurement. As a result of the apparent lack of precision and accuracy of the titration, the alkalinity concentration as calculated from the charge deficit was considered to be a better measure of the true alkalinity than the titration results. Five samples that had large negative charge balances were excluded from the analysis on the basis of very low cation concentrations.

To assess the provenance of sulphate in runoff, samples for the analysis of $\delta^{34}S-SO_4$ and $\delta^{18}O-SO_4$ were collected from the two streams in March 2000 and July 2000 (4 samples total), and a snow sample was collected in March of 2000. Each stream sample was collected in four 1 L polyethelyne bottles (pre-rinsed with DI water, and with sample), and the snow sample was collected in 2 large plastic bags. The samples were kept refrigerated (the snow sample frozen), then passed through anion exchange resins in the laboratory, to concentrate the SO_4^{2-}. The resin columns were shipped to the Environmental Isotope Laboratory, at the University of Waterloo, where the SO_4^{2-} was extracted and the isotopes were analysed on a VG Micromass 602 Dual collector mass spectrometer (for details of methods, see Hemskerk, 1993a; Hemskerk, 1993b).

In 1998, aliquots (250ml) of filtered sample were collected for the measurement of the isotopic composition and dissolved concentration of Sr by isotope dilution thermal ionization mass spectrometry (ID-TIMS). Samples were collected in pre-cleaned polyethylene bottles. The cleaning consisted of triple rinsing in 18.2 MΩ deionised (DI) water, then filling with DI water and letting stand for 3 days, triple rinsing again, and then repeating this rinse-fill-rinse cycle a second time. After collection, samples were acidified with 800μl of 6.2N purified HCl. A specific mass of water (5g for GL samples, 40g for BR samples) from each sample was then accurately weighed and spiked with a known amount of ^{84}Sr tracer solution. The tracer solution was calibrated directly against a solution of the Sr reference material SRM987, and the concentration of ^{84}Sr is known to better than ±0.2%. The spiked solutions were then dried in PFA Teflon at ~ 80°C for 6-18 hours, in Class 100 HEPA filtered air. Chemical separation and mass analysis of Sr used standard cation exchange chromatography and thermal ionization mass spectrometry (Holmden et al., 1996), except that Sr was loaded onto a single rhenium filament with a mixture of hydrous tantalum pentoxide gel and orthophosphoric acid. All the $^{87}Sr/^{86}Sr$ analyses are corrected for variable mass fractionation to $^{87}Sr/^{86}Sr = 0.1194$ and are presented relative to $^{87}Sr/^{86}Sr = 0.710245$ SRM987.

Samples for DOC analysis were filtered on-site using a glass filtration apparatus and Whatman GF/F glass fibre filters. Filtered sample was transferred to amber glass EPA vials, acidified to pH 2 with HCl, and refrigerated until analysis. Prior to sampling, vials were rinsed with DI water and combusted overnight at 550°C. The filtration apparatus was soaked and rinsed with 30% hydrogen peroxide, DI water, and sample between each use. DOC was measured as non-purgeable organic carbon (NPOC) by high temperature combustion (680°C) with a Shimadzu TOC 5000A equipped with high sensitivity platinum catalyst.

Stage in each stream was recorded continuously (hourly averages of pressure sampled every 10 seconds), using a pressure transducer. The pressure record was converted to discharge by calibrating pressure with discharge measured by the velocity-area method. Velocity was measured at a minimum of 15 points in the stream cross-section. Errors on the discharge measurements are estimated to be ±10% (Dingman, 1993). The pressure-discharge calibrations consisted of 8-13 points (usually defining a power relationship in the form of $Q = b \cdot S^a$, where Q is discharge in m^3/s and S is stage or pressure), and the R^2 values for the regressions were between 0.87-0.99, with confidence levels greater than 99.98% ($p<0.0002$). The hourly discharge records (m^3/s) for the two streams are presented in Figure 4.2. Table 4.1 presents the mean snowpack conditions at Bow Summit, and the mean monthly air temperature and precipitation recorded at the Bow Lake meteorological station for the 1997-98, 1998-1999, and 1999-2000 seasons (Figure 4.1).

4.3.2 Flux calculations

The relationship between the concentration (μeq/L) of each dissolved ion and meltwater discharge (m^3/s) was determined by least squares regression (Appendices 2 and 3). The regression equations and continuous discharge records were used to predict continuous (hourly) records of ion concentrations for the periods May 17th to September 4th (or day 137-247) of 1998, 1999 and 2000. The hourly ion fluxes (meq/hr) were calculated from the predicted hourly ion concentration (μeq/L) and discharge (m^3/hr). The hourly fluxes were then summed to determine the summer ion flux (meq). The error on the summer flux was estimated as the quadratic sum (Taylor, 1997) of the uncertainties of the discharge estimates (errors in the discharge measurements and errors in the stage-discharge regression) and concentration estimates (the error in the ion concentration measurements (listed in section 3.1), and the error of the ion-discharge regression). The uncertainties in the summer solute fluxes were between 11-21%, except in the case of nitrate in the Bow River in 1998, for which the uncertainty was 32%.

The average 'winter' flux in each stream was estimated using the average ion concentrations of samples collected between October and April and an estimate of daily mean discharge. As only a limited number of samples were taken during fall and winter, the discharge and solute fluxes were estimated using the means of samples taken during all three years (n = 4 for both GL and BR). The stream gauging stations had to be removed in the fall of each year in order to avoid damage from ice. The daily mean winter discharge was therefore taken to be the lower of the values recorded on the last full day of record in the fall and the first day of record the following spring. It is recognised that this approach likely overestimates the winter solute flux from each catchment.

4.4 RESULTS

Table 4.2 (a, b) lists the summer (May-September), winter (October-April) and annual solute fluxes for BR and GL for 1998, 1999 and 2000. The solute fluxes and discharges in both streams were similar in 1999 and 2000. In 1998, the discharge and fluxes of most solutes in GL were significantly higher than in the other years, while in BR they were lower in 1998 than in subsequent years (Table 4.2a).

The estimated total winter fluxes and discharges were very similar in the two streams. The most significant inter-stream differences in winter fluxes were that Na^+ and HCO_3^- fluxes were higher in BR, while Sr^{2+} and SO_4^{2-} fluxes were higher in GL (Table 4.2a). The winter solute flux constituted 12-17% of the total annual flux in GL, and 24-31% in BR (Table 4.2c). Winter fluxes contributed most significantly (22-26%) to the annual fluxes of Cl^- and SO_4^{2-} in GL, and of NO_3^- (36-72%) and SO_4^{2-} (33-41%) in BR. The contribution of winter flux to annual Sr^{2+} fluxes was substantially lower (16-18%) than for other species of ions in BR (Table 4.2c).

The rest of the paper focuses on the summer fluxes, which are well constrained and most strongly affected by climate-driven changes in runoff and flow routing.

4.4.1 Inter-annual variability of solute fluxes

To facilitate the interpretation of inter-annual changes in solute fluxes relative to changes in discharge, the ratio of the solute fluxes in different years divided by the ratio of the discharges in the same years (i.e. $(F_{1998}/F_{1999})/(Q_{1998}/Q_{1999})$) was calculated (Table 4.3). This parameter is referred to as the 'Flux Change Relative to Discharge'. For consistency, values are calculated by ratioing the year with the higher discharge to the year with lower discharge (Table 4.3). Where the Flux Change Relative to Discharge is <1, the increase in the solute flux between years was less than the increase in discharge, so the additional water led to a dilution of solute concentrations in runoff. If the Flux Change Relative to Discharge is ~1, then the change in solute flux was proportional to the change in discharge. Thus, the additional water was accompanied by a similar addition of solute (either because there was an increase in weathering rates, or because the water source was as concentrated as the stream runoff). Where the Flux Change Relative to Discharge is >1, the increase in the solute flux was greater than the increase in discharge, suggesting either that the additional discharge introduced/accessed a new source of the solute, caused a disproportionate increase in weathering rates, or that there was a decrease in a sink for the solute.

The summer discharge in GL was 1.8 and 2.0 times higher in 1998, than in 1999 and 2000, respectively (Table 4.3). For most ion species, the Flux Change Relative to Discharge in GL for 1998:1999 and 1998:2000 was only 0.7-0.8 (or 70-80%, Table 4.3). There was little difference in either discharge or solute fluxes between 1999 and 2000, for either stream (Table 4.3). In GL, Cl^- and NO_3^- showed the smallest Flux Changes Relative to Discharge for both 1998:1999 and 1998:2000 (0.46-0.55, Table 4.3). Over the 3 years, the fluxes of these 2 ions in GL were virtually independent of variations in discharge (Table 4.2a), so the added runoff in 1998 probably diluted the sources of these solutes in the stream relative to 1999 and 2000. Compared to other major ion species in GL, the Flux Changes Relative to Discharge for Mg^{2+} and SO_4^{2-} were also low (0.60-0.65) for 1998:1999 and 1998:2000 (Table 4.3). This suggests either that these solutes are derived from more resistant lithologies than other solutes (i.e. weathering was rate limited), or that the routing of the additional snow and ice melt gave runoff more limited access to sources of these solute species than to those of other solutes.

The Bow River discharge was 1.5 and 1.3 times higher in 1999 and 2000 than in 1998 (Table 4.3). In contrast to GL, fluxes of K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- in BR increased approximately in proportion with discharge (Table 4.3). The increases in the flux of Sr^{2+} in BR in 1999 and 2000 relative to 1998 were, however, much less than the increases in runoff (i.e. fluxes were diluted by the additional snowmelt input in 1999 and 2000). For NO_3^- and Cl^-, flux increases for 1999:1998 and 2000:1998 were much greater than the corresponding increases in discharge (Table 4.3). This suggests that the increases in BR discharge in 1999 and 2000 either introduced a new source of these solutes, or reduced the removal or retention of these solutes in the BR catchment.

4.4.2 Inter-catchment comparison

Since the Glacial catchment has a larger area than the Bow River catchment, specific solute fluxes (meq/m^2) and discharges (m^3/m^2) were used to compare solute generation in the two catchments (Table 4.4a). The specific flux is the quantity of solute generated per square meter of the catchment, and is also referred to as the denudation rate of a catchment (Anderson et al., 1997). The specific flux of total solute from the GL catchment was more than double that from the BR catchment in 1998, but only marginally higher in 1999 and 2000 (Table 4.4a). The higher specific solute flux in GL relative to BR in 1998 was apparently largely due to the additional discharge, since the specific discharge for GL was much higher than for BR in that year (Table 4.4a). GL also had higher specific discharge than BR in 1999 and 2000, but the two streams had similar specific solute fluxes (Table 4.4a).

Table 4.4b lists the ratios for the specific solute fluxes and specific discharges between the two streams (F_s^{GL}/F_s^{BR} and Q_s^{GL}/Q_s^{BR}) in each of the three years. For Mg^{2+}, Ca^{2+}, and HCO_3^- the ratios of the specific fluxes (F_s^{GL}/F_s^{BR}) were usually approximately equal to or greater than one, but less than the ratios of the specific discharges (Q_s^{GL}/Q_s^{BR}) between the streams (Table 4.4b). This indicates that the higher denudation rates in the GL catchment are due to the higher discharges from this catchment. The only solutes for which the specific flux ratios between the two catchments exceeded the specific discharge ratios were Sr^{2+}, NO_3^-, and SO_4^{2-} (Table 4.4b). For Sr^{2+}, the ratio of the specific fluxes between the two streams was 5-6 times higher than the ratio of the specific discharges in 1999 and 2000, and approximately 3 times higher in 1998 (Table 4.4b). The ratio of the specific fluxes for SO_4^{2-} was approximately 1.3 times greater than the ratio of specific discharge in 1999 and 2000, but was slightly less than the ratio of the specific discharges between the two streams in 1998 (Table 4.4b). For NO_3^-, the specific flux ratios were almost 3 times higher than the ratios of specific discharges for 1999 and 2000, and more than 4 times higher in 1998 (Table 4.4b). This indicates that GL usually generates more Sr^{2+}, SO_4^{2-} and NO_3^- per unit area and unit volume of runoff than BR (i.e. the solute is more concentrated in GL). The ratios of the specific fluxes for Na^+ and K^+ (in 1999 and 2000) and Cl^- (in all years) were less than one (Table 4.4b), indicating that the BR catchment generated much more of these solutes per unit area despite the lower specific discharge. These species were therefore more concentrated in the BR than in GL (Table 4.4 and Table 4.6)

In terms of bulk solute composition, the two streams were very similar. 99% of the total solute flux from both catchments was composed of HCO_3^-, Ca^{2+}, and Mg^{2+}, indicating that carbonate weathering was the dominant weathering reaction in both catchments, despite significant differences in the distribution of carbonate lithologies. However, the relationships between the fluxes of the dominant ions were very different in the two streams. The $Mg^{2+}:Ca^{2+}$ ratios were much lower, and the $(Ca^{2+}+Mg^{2+})/HCO_3^-$ ratios higher in GL than in BR (Table 4.2a).

As illustrated in the preceding analysis, there were also substantial inter-annual and inter-catchment differences in the relative abundance of many of the less abundant ion species, specifically: Na^+, Cl^-, Sr^{2+}, NO_3^-, and SO_4^{2-}.

The influence of solute sources and biogeochemical processes on the behaviour of these species is considered in the next section. Table 4.5 lists the principal weathering reactions anticipated, based on the geology of the catchments.

4.5 DISCUSSION

4.5.1 Solute sources

4.5.1.1 Sulphate

Sulphate may be derived from both atmospheric sources (including natural and anthropogenic) and crustal sources. Atmospheric sources of SO_4^{2-} include seasalt and sulphuric acid (H_2SO_4) aerosols. The average concentration of SO_4^{2-} in the stream runoff (Table 4.6) was, however, more than two orders of magnitude higher than the average snowpack concentration (Table 4.7). This indicates that snowpack derived sulphate could not have represented more than a very small fraction of the total summer SO_4^{2-} flux in these streams.

The potential crustal sources of SO_4^{2-} are pyrite oxidation (Table 4.5, equation 2) and the dissolution of evaporites such as gypsum ($CaSO_4{\cdot}2H_2O$) and/or anhydrite ($CaSO_4$, Table 4.5, equation 4). Pyrite is known to exist throughout many of the formations within the Middle Cambrian carbonates (Atkinson, 1983), whereas evaporites appear to be uncommon within these rocks. Aitken (1997, p.78) notes that gypsum occurs in the Middle Cambrian Mt. Whyte-Cathedral grand cycle, but there is no mention of its abundance or of where it was observed. Although it is unlikely that there are any significant deposits of evaporites in this area, it is likely that there are sulphate bearing evaporites within the Upper and Middle Cambrian dolomites. Dolostones formed from sea water-derived fluids are often associated with considerable amounts of gypsum and/or anhydrite (Machel and Anderson, 1989).

Since, in the presence of bicarbonate, both pyrite oxidation (coupled with carbonate dissolution) and gypsum dissolution require that (Ca^{2+} + Mg^{2+}) be balanced by (HCO_3^- + SO_4^{2-}), the relative importance of the two sets of reactions cannot effectively be determined based solely from the ratios between these ions. The stable isotopes of SO_4^{2-} can, however, usually be used to distinguish between evaporite and sulphide sources because the isotopes of oxygen and sulphur in SO_4 are highly fractionated between compounds during geochemical and/or biological reactions.

The results of $\delta^{34}S$-SO_4^{2-} and $\delta^{18}O$-SO_4^{2-} isotope analysis of SO_4^{2-} from stream and snow samples are presented in Table 4.8.

The sulphate in the snow was depleted in $\delta^{34}S$ relative to the stream sulphate, but the $\delta^{18}O$ was enriched relative to BR sulphate (by ~ +13‰), and similar to the $\delta^{18}O$ of the sulphate in GL. However, since SO_4^{2-} from the snowpack appears to have been a small fraction of the stream SO_4^{2-} load, it is unlikely that the isotopic composition of the snow had any impact on the isotopic ratios of SO_4^{2-} in the streams. The $\delta^{34}S$-SO_4^{2-} in GL is very near the mean for Cambrian marine sulphate values, while the $\delta^{18}O$-SO_4^{2-} is depleted by ~10‰ relative to the average $\delta^{18}O$ of Cambrian marine SO_4. In BR, the $\delta^{34}S$-SO_4^{2-} is depleted by ~11‰ and the $\delta^{18}O$-SO_4^{2-} is depleted by ~ 24‰ relative to Cambrian marine sulphate.

In the case of the Glacial stream, the $\delta^{34}S$ is too enriched for much of the SO_4^{2-} to have been derived from oxidized sulphide minerals (($\delta^{34}S$ –20 to 15‰ CDT, Fig. 6-1,Clark and Fritz, 1997). The $\delta^{18}O$-SO_4^{2-} is, however, too depleted for the SO_4^{2-} to have originated directly from the dissolution of marine evaporites of Cambrian age. The only process that can explain the large reduction in $\delta^{18}O$ with minimal reduction in $\delta^{34}S$ is the biological reduction of SO_4^{2-} to HS^-, followed by the reoxidation to SO_4^{2-} in a nearly closed system (Grasby et al., 2000; van Everdingen et al., 1982). If there is minimal loss of HS^-, the $\delta^{34}S$-SO_4 should not be altered by the biological cycling. Much of the oxygen used during the oxidation of HS^- is, however, derived from water (van Stempvoort and Krouse, 1994). Since the $\delta^{18}O$ of surface water in these catchments in 2000 was on average –20.7±0.4‰ VSMOW (Lafrenière, unpublished data), the reoxidised SO_4^{2-} will be depleted in ^{18}O relative to the original SO_4^{2-} ($\delta^{18}O$ of marine SO_4^{2-} +14‰). The observation that GL obtains most of its sulphate from evaporites contradicts other studies of glacial meltwater from the same Cambrian carbonate formations at other sites in the Rockies, where the dominant source of sulphate was thought to be pyrite oxidation (Atkinson, 1983; Fairchild et al., 1994).

For the Bow River SO_4^{2-}, $\delta^{34}S$ and $\delta^{18}O$ are too reduced for the sulphate to be derived from the simple dissolution of Cambrian marine evaporites. On a plot of $\delta^{18}O$-SO_4 vs. $\delta^{18}O$-H_2O, the $\delta^{18}O$ values for SO_4^{2-} from BR are well within the sulphide oxidation field (van Stempvoort and Krouse, 1994). The $\delta^{34}S$ of +18‰ is, however, at the high end of what would be expected for sulphate derived from sulphide minerals (Clark and Fritz, 1997). These results suggest three possible explanations for the source of SO_4^{2-} in BR: 1) the SO_4^{2-} is primarily from oxidized pyrite that was enriched in $\delta^{34}S$, (2) there is a mix of evaporite and sulphide derived SO_4^{2-}, or (3) there was a mixing of evaporite and sulphide derived SO_4^{2-} as well as some biological cycling of sulphur. The simplest explanation is that the SO_4^{2-} is primarily from the oxidation of pyrite. Although the $\delta^{34}S$ values are somewhat higher than normally expected for sulphide minerals, the $\delta^{34}S$ of pyrite has been shown to vary by as much as 50‰ within a limited region of a single formation (Machel et al., 1995). Without knowing more about the $\delta^{34}S$ composition of pyrite in the catchment, it is therefore difficult to rule out the possibility that the SO_4^{2-} is derived from oxidized pyrite, especially since the $\delta^{18}O$-SO_4 falls within the range of values associated with sulphide oxidation. Yet, it is also possible that the SO_4^{2-} in the Bow River is derived from a mixture of evaporite and sulphide sources. However, the fraction of SO_4^{2-} derived from the dissolution of Cambrian evaporites would still have to be very small, and considerable closed system biological cycling of SO_4^{2-} would be required to explain the large depletion in $\delta^{18}O$ of SO_4^{2-}.

4.5.1.2 Strontium

As with sulphate, the relative concentrations and patterns of variability of strontium in the two streams are very different than those of most other solutes. Strontium is widely dispersed; it replaces calcium in many minerals, and ^{87}Sr is the daughter nuclide in the radioactive decay of rubidium, which substitutes for potassium in K-bearing minerals such as biotite and K-feldspars. Therefore, Sr occurs in a variety of silicate, carbonate and evaporite minerals. Strontium is more than twice as abundant in carbonates as in shales, and generally 10 times more abundant in shales as in sandstones (Turekian and Wedepohl, 1961). Strontium abundance in evaporites is difficult to assess because it depends on the environment of formation (Hanor, 2000), but it is similar to that in carbonates and shales, since Sr^{2+} is a minor component of seawater and can replace Ca^{2+} in anhydrite (Hanor, 2000).

As with sulphate, the flux of Sr^{2+} was always greater in GL (Table 4.2), and the ratios of the specific fluxes of Sr^{2+} between the two streams were many times greater than the ratios of the specific discharges (Table 4.4). However, unlike SO_4^{2-}, Sr^{2+} concentrations in GL were always many times higher than in BR (Table 4.6). This suggests that strontium is derived from different sources in the two catchments. If the Sr^{2+} in both streams was primarily from carbonates, we would expect the Sr^{2+} concentrations in GL and BR to be similar, and possibly higher in BR than in GL, since Ca^{2+}, Mg^{2+} and HCO_3^- concentrations are higher in BR than in GL (Table 4.6). A correlation matrix for the concentrations of the major cations and anions shows that, in GL, Sr^{2+}

is most strongly correlated with SO_4^{2-}, and then with Mg^{2+} and Ca^{2+} (Table 4.9a). This suggests either that Sr^{2+} and SO_4^{2-} in GL were derived from the same source (evaporite minerals), or that Sr^{2+} was derived from the same host rocks as the evaporite minerals -the Cambrian carbonates. The correlation between Sr^{2+} and other solutes was much weaker in BR (Table 4.9b). The weaker correlation may be partly due to the fact that the Sr^{2+} concentrations in BR were very low (0-5 $\mu eq \cdot L^{-1}$), relative to GL (5.1-24.8 $\mu eq \cdot L^{-1}$). A larger portion of the variability in Sr^{2+} was therefore likely related to the error in the measurement of Sr^{2+} in BR. The only ions that have significant correlations with Sr^{2+} in BR are SO_4^{2-} and K^+ (Table 4.9b). The correlation between Sr^{2+} and SO_4^{2-} suggests that some Sr^{2+} may be derived from rocks containing pyrite (the dominant source of sulphate in BR), or that the acidity from pyrite oxidation is driving weathering of minerals from which Sr^{2+} is derived. The weak, but significant ($p<0.05$), correlation with K^+ suggests some of the Sr^{2+} in this stream may be derived from K-bearing silicate minerals. The higher K^+ concentrations in BR (Table 4.6), relative to GL suggest that K-bearing minerals may be a more important source of Sr^{2+} in this catchment. Since both pyrite and K-bearing clay minerals such as micas (biotite and muscovite) are normally abundant in shales, it is likely that shales are the dominant source of Sr^{2+} in BR.

This suggestion is supported by the isotopic composition of Sr^{2+} in the two streams. The $^{87}Sr/^{86}Sr$ ratios of Sr^{2+} in the streams are clearly distinct, with BR having higher $^{87}Sr/^{86}Sr$ ratios (0.71622 ± 0.00025) than GL (0.71008 ± 0.00008, Table 4.10). There is almost no change in the isotopic composition between May and August in either stream, although there is a strong correlation between $^{87}Sr/^{86}Sr$ and Sr^{2+} concentration in GL (Table 4.10, Figure 4.3). Carbonates and evaporites contain high concentrations of Sr with low $^{87}Sr/^{86}Sr$, and silicate rocks typically have lower Sr concentrations, but higher $^{87}Sr/^{86}Sr$ ratios. The $^{87}Sr/^{86}Sr$ of GL is higher than is typical (0.7089-0.7094) for Cambrian seawater (Burke et al., 1982; Montañez et al., 2000). However, $^{87}Sr/^{86}Sr$ of dolomite and calcite within the Cathedral Formation of the Cambrian carbonate units in the region ranges from 0.709 to 0.712 (Koffyberg, 1994; Nesbitt and Muehlenbachs, 1994). The high $^{87}Sr/^{86}Sr$ values in these formations are attributed to hydrothermal fluids that reset the Sr signatures of the Cambrian limestones and produced the epigenetic dolomites (Koffyberg, 1994; Nesbitt and Muehlenbachs, 1994). Values for host rocks within the Upper Proterozoic Miette Group averaged 0.7345±0.0014 for limestones (n=2), 0.767±0.016 for slate (n=2), and 0.752±0.014 (n=9) for calcite from vein carbonates.

These $^{87}Sr/^{86}Sr$ values and the correlations between Sr^{2+} concentrations and those of other ions suggest that the Cambrian carbonates (or evaporites within these units), which have high Sr abundance but low $^{87}Sr/^{86}Sr$ ratios, are likely the primary source of Sr^{2+} in GL, while BR derives strontium primarily from rocks containing more radiogenic Sr at lower Sr abundances. The $^{87}Sr/^{86}Sr$ of Sr^{2+} in BR is slightly higher than that of Sr from Cambrian Carbonates, and substantially lower than values derived from rocks and minerals within the Miette Group. The low concentrations of Sr^{2+} in BR suggest that although the Cambrian carbonates may contribute Sr^{2+} to this stream, it is likely a very small fraction of Sr^{2+}, and that there is some mixing with Sr from a more radiogenic source (probably from the Miette or Gog groups). However, it is highly probable that the source of Sr in BR is silicate minerals, but that the $^{87}Sr/^{86}Sr$ released during silicate weathering in BR does not match that of Sr in the source mineral(s). Several laboratory studies of K-silicate weathering have shown that the $^{87}Sr/^{86}Sr$ of weathering solutions can be either higher or lower than that of the minerals being weathered, and that the $^{87}Sr/^{86}Sr$ can change over time (Brantley et al., 1998; Taylor et al., 2000).

4.5.1.3 Sodium and Chloride

In catchments lacking halite in bedrock, it is usually assumed that chloride is derived entirely from atmospheric sources (mainly seasalt aerosol). Since chloride does not participate in biogeochemical, weathering, or ion exchange reactions, it is generally regarded as a conservative solute. Conversely, sodium may be derived from both atmospheric and crustal sources, and it is involved in weathering and ion exchange reactions. The principal crustal source of Na^+ is the weathering of aluminosilicate minerals (Table 4.5, equation 5), but Na^+ may also be derived from carbonate sources (aragonite and Mg-calcite bear significant Na; Fairchild et al., 1994). Sodium is, however, generally much less abundant in waters draining carbonate catchments (1-5% of total cations), than in streams from sandstone and shale catchments (13-45% of total cations,Meybeck, 1987). Sodium and chloride may also be derived from the dissolution of halite (Table 4.5, equation 7). There are, however, no known deposits of halite in the geological formations in the study area, and $Na^+:Cl^-$ ratios are much greater than 1 in these streams (Table 4.6). Hence, it seems unlikely that dissolution of bedrock halite is a major source of solute.

The concentrations of Cl^- in the winter runoff from the two catchments were very similar, but the average winter Na^+ concentration in BR was more than double that in GL (Table 4.6). The higher $Na^+:Cl^-$ in winter runoff in BR suggests that groundwater in this catchment derives much more sodium from rock weathering than does groundwater in the GL catchment. This might be the result of (a) a longer residence time of groundwater in the Bow River catchment, as indicated by the higher concentrations and specific fluxes of Ca^{2+}, Mg^{2+} and HCO_3^- (Table 4.3 and 4.6); and/or (b) more Na^+ derived from the weathering of silicate minerals (such as alkali feldspars). This is expected given the relative abundance of non-carbonate rock in the BR catchment (Figure 4.1).

Although it is not surprising that BR had higher Na^+ concentrations than GL, it is curious that unlike most other solutes, the summer fluxes of Na^+ and Cl^- in 1999 and 2000 were higher in BR than in GL (Table 4.2). The high Flux Changes Relative to Discharge for Na^+ and Cl^- in BR for 1999:1998 and 2000:1998, suggest that a source of Na^+ and Cl^- was introduced or accessed as a result of the additional runoff. In contrast, the Flux Changes Relative to Discharge for Na^+ and Cl^- in GL for 1998:1999 and 1998:2000 were < 1 (Table 4.3), indicating that, in GL, Na^+ and Cl^- concentrations were diluted by the additional discharge in 1998 (Table 4.6).

Seasonal variations in Na^+ and Cl^- concentrations indicate that the additional fluxes of Na^+ and Cl^- from BR in 1999 and 2000 were due in large part to the high concentrations of these ions during the early stages of snowmelt (Figure 4.4). In 1998, when snowmelt occurred prior to the start of sampling, the Na^+ and Cl^- concentrations were relatively constant in both GL and BR throughout the duration of the sampling period, with slight increases in concentrations in the fall (Figure 4.4a). However, in 1999 and 2000, Na^+ and Cl^- concentrations in BR increased dramatically during the very early stages of snowmelt (~ days 120-140 Figures 4.4b and 4.4c). Early season Na^+ and Cl^- concentrations in BR were between 2-3 and 13-29 times higher, respectively, than fall and/or winter concentrations in 1999 and 2000 (Figures 4.4b and 4.4c). Meanwhile, in GL Na^+ and Cl^- concentrations were relatively constant throughout the summers in 1999 and 2000, similar to 1998 (Figures 4.4b and 4.4c).

There are three possible explanations for this dramatic increase in Na^+ and Cl^- concentrations in the Bow River during the early melt season:

(1) the preferential elution of ions from the snowpack giving rise to high solute concentrations in the first fraction of snowmelt,

(2) the flushing of more concentrated soil or shallow groundwaters at the onset of snowmelt, or

(3) input of Na^+ and Cl^- from salt contained in sand applied to Highway 93 (Figure 4.1).

The first fraction of snowmelt is usually the most concentrated as a result of the preferential elution of solutes during snowmelt (Jenkins et al., 1993). If, however, preferential elution were responsible for increases in Na^+ and Cl^- in BR, similar seasonal trends would also be expected in GL. Increases in the Na^+ and Cl^- concentrations in snowmelt collected from beneath the snowpack would also be expected. There is little evidence of increases in Na^+ and Cl^- concentrations in GL during snowmelt in 1999 and 2000 (Figures 4.4b and 4.4c). Furthermore, although the Na^+ and Cl^- concentrations in snowmelt collected from a snowmelt lysimeter in BR catchment in 2000 peaked at approximately the same time as concentrations in runoff (day 123, April 22nd), the concentration increases in snowmelt were relatively minor (Figure 4.4 and 4.5). Maximum Cl^- concentrations in the snowmelt were an order of magnitude lower than the maximum concentrations observed in BR, and the maximum Na^+ concentrations in snowmelt were less than a third of those in BR in 2000 (Figures 4.4c and 4.5). The concentration of ions in the first fraction of the snowmelt cannot, therefore, explain the magnitude of the increases in Na^+ and Cl^- concentrations observed in BR.

Increases in the concentration of certain solutes can occur when soil waters, or concentrated shallow groundwaters, are flushed at the onset of snowmelt. For example, increases in dissolved organic carbon (DOC) concentrations in spring runoff in alpine streams, are attributed to the flushing of dissolved organic matter from catchment soils (Boyer et al., 1997). However, the concentrations of Na^+ and Cl^- observed in the early spring runoff, were many times higher than the concentrations measured in stream runoff in winter or fall (Table 4.6, Figure 4.4). Since stream runoff in winter or fall should consist primarily of groundwater, it seems unlikely that the dramatic increases in Cl^- and Na^+ in the spring were the result of additional groundwater inputs. Soil solutions may potentially contain higher concentrations of solutes than groundwater as a result of evaporative concentration as soils dry out over the summer. DOC concentrations in the Bow River have been observed to increase dramatically during the early stages of snowmelt, as a result of the flushing of catchment soils (Chapter 3). The peaks in Na^+ and Cl^- concentrations (Figure 4.4) are not, however, coincident with the DOC flush from the soils in 1999 and 2000 (Figure 4.6). The flushing of DOC from soil waters in the catchment occurs 12-14 days after the maximum Na^+ and Cl^- concentrations, and the peak DOC concentrations coincide with decreasing solute concentrations (Figure 4.6). Furthermore, if waters containing high concentrations of Na^+ and Cl^- were being flushed from the soils, other solutes should exhibit similar increases in concentrations (Stottlemeyer and Toczydlowski, 1999). Calcium concentrations in BR display seasonal variations similar to Na^+ and Cl^- (Figure 4.6), but the peak Ca^{2+} concentrations in the spring are only approximately 3-10% higher than the fall and winter concentrations, whereas Na^+ and Cl^- concentrations increase by factors of 2-3 and 13-29, respectively. Potassium does not display the same seasonal trends as Na^+ or Cl^- in 1999 and 2000, and maximum K^+ concentrations are only 10-15% higher than fall and winter concentrations (Figure 4.6). It therefore seems unlikely that soil pore waters were the source of the elevated Na^+ and Cl^- concentrations in 1999 and 2000.

Anthropogenic inputs of Na^+ and Cl^- (other than those already accounted for by atmospheric deposition in snow) should be minimal, since the catchments are within a National Park. During the winter months, however, sand which contains 4% NaCl is applied to the Ice Fields Parkway (Douglas Kerr, Parks Canada, pers. comm.), a major road within the Bow River catchment (Highway 93, in Figure 4.1). The Na^+ and Cl^- concentrations in snows from the BR catchment were similar to those in snows from the GL catchment (Table 4.7), which suggests that there was no salt contamination in the snow at the Bow River sampling site (Figure 4.1). It is, however, possible that salt from areas closer to the road contributes Na^+ and Cl^- to the stream solute load during the early part of snowmelt. Given the amplitude of the observed changes in Cl^- and Na^+ concentrations, the lack of a similar increase in the Glacial stream, and the low Na^+:Cl^- ratios at peak concentrations, an input of NaCl from sand applied to the Parkway seems to be the most likely explanation for the changes observed in this stream.

4.5.1.4 Nitrate

Snowpack nitrate originates almost solely from atmospheric deposition. Both wet and dry deposition of nitrate, ammonium (NH4+) and nitric acid are important sources of snowpack nitrate (Cress et al., 1995; Rusch and Sievering, 1995). Possible fates of NO_3^- in the snowpack might include loss by volatilization of NH_3 (Wolff, 1995) and nitrate reduction (by biological assimilation or denitrification). There is also the potential for NO_3^- production within the snowpack by nitrification (biological oxidation of NH_4^+). However, results from several studies of inorganic N in alpine snows show that there is no appreciable transformation (loss or gain) of either NH_4^+ or NO_3^- in the snowpack (Brooks et al., 1993; Williams et al., 1996; Williams and Melack, 1991). Sublimation experiments on freshly fallen snow (Cragin and McGilvary, 1995) also indicate that evaporation of nitrate from the snowpack is minimal. There is some evidence of re-emission of nitrate from snow in polar regions, possibly as a result of photochemical degradation or volatilization (Neubauer and Heumann, 1988). There are, however, many factors that determine the effectiveness of these processes (e.g. air temperature, solar zenith angle, snow accumulation rate, atmospheric concentrations of nitric acid, ventilation of the snow pack, Wolff, 1995). It is therefore difficult to determine whether they are likely to have a significant impact on snowpack nitrate budgets outside the Polar Regions. It is, therefore, assumed that the bulk of nitrate deposited in the Bow Lake catchment is conserved within the snowpack, until it is transferred to the soil zone via meltwater infiltration, or to streams via overland flow.

The balance of gains by atmospheric deposition to the snowpack and N mineralization (ammonification and nitrification) in soils, and losses due to NO_3^- assimilation and denitrification in soils, determines the flux of NO_3^- in runoff. Several studies indicate that the delivery of nitrate to surface waters from the snowpack in high elevation ecosystems is controlled primarily by the balance of soil microbial processes (mineralization versus assimilation/denitrification) beneath the snowpack prior to snowmelt (Brooks et al., 1999; Brooks and Williams, 1999; Heuer et al., 1999; Williams et al., 1996). The level of heterotrophic microbial activity in alpine ecosystems appears to be related to the severity of soil frost and the duration of the period for which the soil is thawed (Brooks and Williams, 1999). A short period of snow cover limits heterotrophic activity beneath the snow, while prolonged and deep snow cover allows microbial activity to continue in thawed soils throughout the winter (Brooks and Williams, 1999). Freeze-thaw cycles can also enhance microbial activity, by providing a labile carbon substrate for microbial assimilation once soils beneath the snowpack thaw (Brooks and Williams, 1999). Brooks and Williams (1999) found that deep consistent snowpack increased microbial activity (N_2O flux from subnival soil) and microbial biomass, but reduced NO_3^- export from the catchment relative to shallow, inconsistent snow cover. In other words, the deeper snowpack resulted in greater use (assimilation/denitrification) of NO_3^- by soil microbes relative to the release of NO_3^- from mineralization. In contrast, another study of N cycling in alpine catchments found higher stream nitrate concentrations and lower inorganic nitrogen retention during years with deep/late melting snowpack (Sickman et al., 2001). This was attributed to the combination of lower NO_3^- uptake by plants due to longer snow-lie, and greater production of labile N in soils, because N mineralization and nitrification in snow covered soils continued later into the spring (Sickman et al., 2001; Sickman et al., in press). In general, soils do not contribute significant amounts of nitrate to streams after the snowmelt runoff period (Campbell et al., 1995; Williams et al., 1996). In the absence of rain, the input of water to soils ceases and shallow sub-surface flow to streams is limited (Campbell et al., 1995). As spring progresses, the nitrate in organic soils is usually assimilated or denitrified by microbial biomass, or taken up by vegetation during the growing season (Campbell et al., 1995).

Nitrate fluxes were always an order of magnitude higher in GL than in BR (Table 4.2). The seasonal average NO_3^- concentrations in the streams were approximately 2-4 $\mu eq \cdot L^{-1}$ in BR, and 4-8 $\mu eq \cdot L^{-1}$ in GL (Table 4.6). Nitrate concentrations in the snow at Bow Lake were between approximately 3-5 $\mu eq \cdot L^{-1}$, and $NO_3^-:Cl^-$ ratios were 2-4 (Table 4.7). Assuming that Cl^- behaves conservatively, then the difference in the $NO_3^-:Cl^-$ ratio between the snow and the streams is an indication of the effect of catchment processes on NO_3^- export to the streams. The $NO_3^-:Cl^-$ ratios in GL (1.7-2.0) were similar to the ratios observed in snows (Table 4.7), while the $NO_3^-:Cl^-$ ratios in BR were always substantially lower than in the snow (Table 4.6 and 4.7). Although elevated Cl^- concentrations resulting from anthropogenic sources of salt may have lowered the $NO_3^-:Cl^-$ ratios in BR in 1999 and 2000, the ratio was even lower in 1998 (when Cl^- appeared to be unaffected by salt contamination, Figure 4.4a) than in 1999 and 2000 (Table 4.6). Furthermore, the $NO_3^-:Cl^-$ ratio for GL was higher in the summer than in the winter, while the opposite was true for BR (Table 4.6). These results suggest that the Glacial catchment may be a source of NO_3^- to the stream during the spring and summer, while the Bow River catchment appears to act as a sink for NO_3^-.

The higher flux and concentration of NO_3^- from GL (i.e. lower catchment retention of NO_3^-) relative to BR may be largely due to differences in the extent of soil and vegetation cover in the two catchments. Several recent analyses of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rocky Mountains, have found that the yield of dissolved inorganic nitrogen (DIN, i.e. $NH_4^+ + NO_3^-$) decreased with increasing soil cover, while the DIN retention increased (Sickman et al., 2002; Sueker et al., 2001). One study found that log-linear regression models using soil cover as the independent variable explained 82% and 90% of the variation in DIN retention between alpine catchments in the Sierra Nevada and Rocky Mountains, respectively (Sickman et al., 2002).

The seasonal variation in NO_3^- relative to DOC (which is flushed from catchment soils during snowmelt, Chapter 3), also suggests that the flow routing of runoff through soils results in a decrease in NO_3^- concentrations (Figure 4.7). When DOC concentrations increased during the first stages of snowmelt, NO_3^- concentrations in BR decreased substantially in 1999 and 2000. In BR, NO_3^- also tends to vary inversely with DOC over the rest of the summer, suggesting that when runoff is flushing DOC from soils, it is losing NO_3^- (Figure 4.7). In GL, NO_3^- generally increased with DOC during snowmelt, except occasionally during the later stages of snowmelt (Figure 4.7, 1998 (days 150-175) and 1999 (days 165-175)). This suggests that NO_3^- in snowmelt is largely unaffected by contact with soils in the GL catchment.

The higher than snowpack NO_3^- concentrations in GL suggest that the Glacial catchment may be a source of NO_3^-. This might also have to do with the lack of vegetated soils in this catchment. Williams et al. (1997) found that the fine sediments under talus fields 'subtalus soils' supported microbial activity, and that NO_3^- in talus fields may contribute NO_3^- to stream waters in high elevation catchments. The subtalus soils contained similar amounts of extractable NH_4^+ and NO_3^- as well developed, vegetated soils. They contained much less microbial biomass, however, suggesting that inorganic N was rapidly assimilated in vegetated soils, but inorganic N production exceeded assimilation and uptake by plants and microbes in the subtalus soils (Williams et al., 1997). The role of steep slopes and unvegetated terrain in elevating NO_3^- concentrations in alpine streams has also been noted in other studies (Campbell et al., 2000; Sueker et al., 2001). Nitrate concentrations in soil waters collected from tension lysimeters from 4 sites around Bow Lake also suggest that unvegetated, and poorly developed soils represent potential sources of NO_3^- in the catchment (Table 4.11). Nitrate concentrations in soil waters were much higher in the 2 sites where there was little vegetation and poorly developed soils (BR-S2, GL-S1), than in the 2 sites where there were was vegetation and well defined soil structure (BR-S1, GL-S2, Table 4.11). The details of the soil lysimeter locations and sampling methods are described in Chapter 3.

Nitrate concentrations and fluxes in BR increased with runoff and snow depth (Table 4.2 and 4.6). The NO_3^-:Cl ratio also increased in 1999 and 2000 relative to 1998 (despite the significant increases in Cl fluxes), which suggests that the catchment was less of a NO_3^- sink in 1999 and 2000 than in 1998. The Flux Changes Relative to Discharge for both 1999:1998 and 2000:1998 also indicate that there was a decrease in the removal (or else an added source) of NO_3^- in 1999 and 2000 compared to 1998 (Table 4.3). In GL, nitrate fluxes were virtually unaffected by inter-annual changes in runoff. Even though the 1998 runoff was almost double that in 1999 and 2000, nitrate flux from the catchment was virtually unchanged (Table 4.2). The increased discharge in 1998 resulted in lower mean seasonal NO_3^- concentrations (Table 4.6) than in years with lower discharges.

The lower NO_3^- concentrations observed in GL runoff in 1998 are to be expected. Increased ice ablation in the summer should result in a dilution of NO_3^- in the stream, because ice and firn are depleted of solute as a result of the leaching of NO_3^- from snow (Fountain, 1996; Tranter et al., 1993). The observation that the BR catchment is a sink for NO_3^-, but that the sink is less effective in high snowfall/high runoff years is consistent with results from other studies of nitrogen in high elevation catchments in the Sierra Nevada (Sickman et al., 2001; Sickman et al., in press). Sickman et al. (2001) attribute the higher NO_3^- flux to greater mineralization, and less uptake by plants because of the longer snow lie. However, the relative increases in NO_3^- during high snowfall years could also be hydrologically controlled. For example, the larger volume of water contained in the deeper snowpack, could mean that a lower the proportion of available water (and solute) is required to bring soils to saturation, resulting in a greater proportion of snowmelt runoff occurring as overland flow. If this were the case in the BR catchment, then a smaller proportion of the snowpack nitrate would infiltrate the soil zone when runoff is high, resulting in a greater export of nitrate, since less is available for biological uptake in the soils.

The results of this study therefore indicate that the lower NO_3^- concentrations and fluxes in BR are largely due the much greater soil covered area in this catchment, and that the greater water volume, and/or longer snow lie from the deeper snowpack and cold temperatures in 1999 and 2000 resulted in an increase the fraction of NO_3^- exported (decrease in the removal of NO_3^-) from the BR catchment. A more extensive study of NO_3^- dynamics in the area would be required to determine exactly how snow depth and duration affect the various processes controlling the export of nitrate from the BR catchment.

4.5.2 Solute flux variations

Runoff was the dominant control on the inter-annual variations in total solute flux, with solute flux in both streams increasing with discharge. However, since the two streams exhibited opposite discharge responses to changes in climate, they also displayed opposite solute flux changes between years. Thus, for the 1998 El Niño year, when winter precipitation was low and summer temperatures were high, runoff and fluxes from BR were low, and those for GL were high relative to 1999 and 2000, when winter snowfalls were higher and spring/summer temperatures were cooler (Table 4.1 and 4.2).

The Glacial stream had higher chemical denudation rates (specific solute flux) than BR, in any given year (Table 4.2 and 4.4). The higher chemical denudation rates in the GL catchment seem to be primarily the result of higher specific discharge in GL. As a result of the opposite discharge responses to the lower snowfall in the winter of 1997/1998, the difference in the total seasonal solute flux between the two catchments was greatest in 1998. BR always had higher solute concentrations than GL, even though it drained a catchment containing abundant silicate minerals that are generally more resistant to weathering than carbonates. The greater solute generation per unit of water in the BR catchment is likely due to a combination of catchment processes, such as the provision of protons from pyrite oxidation, or carbonic and organic acids from the soils (Drever, 1997), and longer water:rock contact times (for example as a result of significant routing of water through groundwater and soils), and possibly concentration by evapotranspiration (White and Blum, 1995). These results are consistent with the findings of Anderson et al. (1997) that glacier covered catchments produced higher cation fluxes compared to non-glacial catchments of the same rock type, but that the high denudation rates in glacier-covered catchments were a consequence of higher water fluxes.

In 1998 there was a substantial increase in the seasonal solute flux from GL relative to 1999 and 2000 (except for Cl^- and NO_3^-, which are not derived primarily from mineral weathering, see Table 4.2), but the increase was only 70-73% of the increase in discharge (Table 4.3). Thus, mineral dissolution did not keep pace with the increase in discharge and solute concentrations were reduced. This likely reflects changes in the flow routing, water:rock contact time and mineral surface area to water volume ratios resulting from the substantial glacial ablation and the development of subglacial channels in the summer of 1998 (Lafrenière and Sharp, 2003). The slow transit of waters through a distributed subglacial drainage system (which likely dominated in 1999 and 2000, Lafreniere and Sharp, 2003) promotes relatively efficient chemical weathering compared to weathering in a well developed channelised subglacial system (Tranter et al., 1993). The stronger dilution of Cl^- and NO_3^- (i.e. the low Flux Change Relative to Discharge, Table 4.3) are expected under conditions of increased glacial ablation, since these solutes are not derived from mineral weathering, and snowmelt derived solutes would be diluted by ice melt. The crustally derived ions that experienced the lowest flux increases in 1998 relative to 1999 and 2000 were SO_4^{2-} and Mg^{2+}. The low Flux Change Relative to Discharge for SO_4^{2-} and Mg^{2+} (Table 4.3) suggest that the dissolution of sulphate (from evaporites) as well as magnesium (from dolomites) in the Glacial catchment is constrained by either the spatial distribution of source minerals relative to runoff, or their dissolution kinetics, under the high discharge conditions. Evaporite minerals, the likely source of SO_4^{2-} in this catchment, are almost certainly associated with the dolomites in the Cambrian carbonate units (Machel and Anderson, 1989; Nesbitt and Muehlenbachs, 1994). Since gypsum and anhydrite have high solubilities, the relatively low flux of SO_4^{2-} is most likely related to the distribution or rate of dissolution of the host dolomites. Dolostones are present within outcrops surrounding the Wapta Icefield, and Bow Glacier (Price and Mountjoy, 1978), therefore there is no reason to suspect that the distribution of dolomite in the subglacial environment is limited, although it may be limited relative to the flow of water in channels. Hence the limited provision of SO_4^{2-} and Mg^{2+} relative to the other major solutes in 1998 is likely due to the slow dissolution of dolomite (and thus evaporites within the dolomites), and the shorter residence time of runoff under conditions of high ablation and channelised subglacial drainage.

In BR, the total solute flux increases in 1999 and 2000 relative to 1998, were approximately proportional (97-99%) to the increases in discharge (Table 4.3). Analysis of the runoff regime of BR between 1998 and 2000 indicates that the flow routing of melt water was faster/more efficient in 1998 than in 1999/2000 (Lafrenière and Sharp, 2003). This suggests that slower flow routing in the catchment in 1999 and 2000, enabled weathering rates to keep pace with the increases in the volume of runoff. The additional snowmelt may also have increased weathering rates by flushing more protons from carbonic and organic acids from the soils.

4.6 CONCLUSIONS

This study shows that adjacent glacial and non-glacial catchments experience opposite solute flux responses to climate perturbations such as ENSO. El Niño conditions (low winter snowfall and warm summer and spring air temperatures) led to increases in the flux of solutes from the glacial catchment, and decreases in the solute flux from the snowmelt fed catchment, relative to La Niña conditions. Inter-catchment differences in solute composition were primarily controlled by differences in catchment geology and the presence of soils, while differences in total solute fluxes were largely dependant on specific discharge. Waters from the Bow River stream have had greater contact with both minerals and organic soils than those from the Glacial stream. The higher chemical denudation rates in the Glacial catchment seem to be primarily due to the high rates of flushing (high discharge), and the higher overall concentration of solutes in the Bow River is likely the result of both longer average water:rock contact (i.e. as a result of larger inputs from groundwater and soil water to runoff), and a greater supply of protons from organic soils and/or pyrite oxidation

The lower contribution from solutes derived from (or dependant on) kinetically slow weathering reactions in the glacial stream during the 1998 El Nino year, indicates a reduction in the average water:rock contact time in the catchment with increases in glacial ablation and the development of subglacial channels, relative to seasons when the subglacial drainage system was likely primarily distributed (Lafrenière and Sharp, 2003). There was also a decrease in the relative importance of atmospherically derived (Cl^- and NO_3^-) solutes with increases in glacially derived runoff. Inter-annual changes in inputs of snowmelt runoff in the non-glacial stream results in a proportional increase in solute flux (i.e. concentrations of most solutes are virtually unchanged), indicating that in this catchment the addition of dilute runoff results in an increase in weathering rates (likely due to increased input of protons from carbonic and organic acids). However, increases in snow/snowmelt runoff appear to reduce the contact of meltwater with soils or biologically active environments, or else reduce the removal of nutrients in these environments by reducing net biological uptake.

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Table 4.1 Snowpack depth (in mm of Snow Water Equivalent; SWE), mean monthly air temperature and rainfall recorded at the Bow Lake meteorological station for 1997-98, 1998-1999, and 1999-2000.

Snowpack (mm SWE) at Bow Summit (2080 masl)	1997-98	1998-99	1999-2000
March 30	257	460	434
May 30	0	329	239
Exhaustion of snowpack at Bow Lake Met Station (1940 masl)	May-02	May-30	May-23
Mean Air Temp (°C)	1998	1999	2000
May	5.5	0.9	1.3
June	6.8	5.3	6.0
July	12.6	7.8	9.6
Aug	11.1	10.5	8.6
Total Rain (mm) May-August	266	263	155

Table 4.2 Measured solute fluxes for the Glacial stream and the Bow River: (a) Summer (May-September) solute fluxes for 1998, 1999 and 2000, and estimated average Winter (October – April) solute fluxes, (b) Annual solute fluxes 1998-2000, and (c) Winter flux as a fraction of annual flux 1998-2000.

Summer and Winter Fluxes (meq/season)

	Discharge Q (m^3)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total	Mg^{2+}:Ca^{2+}	$(Ca^{2+}+Mg^{2+})/HCO_3^-$
GL 1998	3.93E+07	3.01E+08	1.45E+08	1.61E+10	3.25E+10	3.13E+08	6.25E+07	1.45E+08	8.69E+09	4.00E+10	9.83E+10	0.50	1.22
GL 1999	2.13E+07	2.21E+08	1.05E+08	1.44E+10	2.23E+10	2.18E+08	7.43E+07	1.43E+08	7.28E+09	3.12E+10	7.60E+10	0.65	1.18
GL 2000	1.99E+07	2.21E+08	9.30E+07	1.34E+10	2.00E+10	2.23E+08	6.05E+07	1.46E+08	7.39E+09	2.66E+10	6.82E+10	0.67	1.25
GL Winter	2.41E+06	4.78E+07	1.72E+07	3.01E+09	3.84E+09	5.24E+07	2.09E+07	1.96E+07	2.55E+09	4.38E+09	1.39E+10	0.78	1.56
BR 1998	6.47E+06	1.79E+08	5.15E+07	6.52E+09	8.13E+09	1.60E+07	4.46E+07	5.36E+06	1.91E+09	1.29E+10	2.97E+10	0.80	1.14
BR 1999	9.64E+06	3.08E+08	7.59E+07	9.54E+09	1.19E+10	1.97E+07	9.05E+07	2.39E+07	2.71E+09	1.93E+10	4.40E+10	0.80	1.11
BR 2000	8.66E+06	2.58E+08	6.54E+07	8.16E+09	1.04E+10	1.62E+07	8.53E+07	2.29E+07	2.40E+09	1.74E+10	3.88E+10	0.79	1.07
BR Winter	2.12E+06	9.01E+07	1.97E+07	3.11E+09	3.51E+09	3.63E+06	1.94E+07	1.37E+07	1.34E+09	5.35E+09	1.34E+10	0.89	1.24

Annual Fluxes (meq/yr)

	Q (m^3)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total
GL 1998	4.17E+07	3.54E+08	1.63E+08	1.92E+10	3.64E+10	3.67E+08	8.47E+07	1.65E+08	1.13E+10	4.43E+10	1.12E+11
GL 1999	2.37E+07	2.74E+08	1.22E+08	1.75E+10	2.61E+10	2.72E+08	9.65E+07	1.62E+08	9.94E+09	3.56E+10	8.99E+10
GL 2000	2.23E+07	2.74E+08	1.11E+08	1.64E+10	2.39E+10	2.77E+08	8.27E+07	1.65E+08	1.00E+10	3.10E+10	8.22E+10
BR 1998	8.59E+06	2.69E+08	7.12E+07	9.63E+09	1.16E+10	1.97E+07	6.40E+07	1.91E+07	3.25E+09	1.82E+10	4.33E+10
BR 1999	1.18E+07	3.08E+08	9.56E+07	1.26E+10	1.54E+10	2.34E+07	9.05E+07	3.76E+07	4.04E+09	2.46E+10	5.78E+10
BR 2000	1.08E+07	3.48E+08	8.51E+07	1.13E+10	1.39E+10	1.99E+07	1.05E+08	3.66E+07	3.74E+09	2.27E+10	5.14E+10

Winter flux as a fraction of Annual flux

Glacial	Q (m^3)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total
1998	0.06	0.14	0.11	0.16	0.11	0.14	0.25	0.12	0.23	0.10	0.12
1999	0.10	0.18	0.14	0.17	0.15	0.19	0.22	0.12	0.26	0.12	0.16
2000	0.11	0.18	0.16	0.18	0.16	0.19	0.26	0.12	0.26	0.14	0.17
Bow River											
1998	0.25	0.33	0.28	0.32	0.30	0.18	0.30	0.72	0.41	0.29	0.31
1999	0.18	0.23	0.21	0.25	0.23	0.16	0.18	0.36	0.33	0.22	0.23
2000	0.20	0.26	0.23	0.28	0.25	0.18	0.19	0.37	0.36	0.24	0.26

Table 4.3 Flux Change Relative to Discharge [$(F_{1998}/F_{1999})/(Q_{1998}/Q_{1999})$] for the Glacial and Bow River streams. The discharge column (Q) shows that ratio of the discharges for the years specified (e.g. Q_{1998}/Q_{1999}). The solute columns show the Flux Change Relative to Discharge.

	Q (m^3)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total
GL											
1998:1999	1.8	0.74	0.75	0.61	0.79	0.78	0.46	0.55	0.65	0.70	0.70
1998:2000	2.0	0.69	0.79	0.61	0.82	0.71	0.52	0.50	0.60	0.76	0.73
1999:2000	1.1	1.00	1.13	1.08	1.11	0.98	1.23	0.98	0.99	1.17	1.11
BR											
1999:1998	1.5	1.15	0.99	0.98	0.98	0.82	1.36	3.00	0.95	1.01	0.99
2000:1998	1.3	1.08	0.95	0.93	0.95	0.76	1.43	3.19	0.94	1.01	0.97
1999:2000	1.1	1.07	1.04	1.05	1.03	1.09	0.95	0.94	1.01	1.00	1.02

Table 4.4 (a) Seasonal discharge (m^3), specific discharge (Q_s, m^3/m^2) and specific ion fluxes (F_s, in meq/m^2) for the Glacial stream and Bow River. (b) The ratios of specific water and solute fluxes between the Glacial stream and the Bow River (Q_s^{GL}/Q_s^{BR} and F_s^{GL}/F_s^{BR}) for 1998, 1999 and 2000.

(a)

	Q (m^3)	Specific Q (m^3/m^2)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total
GL 1998	3.93E+07	1.45	11	5.4	597	1204	12	2.3	5.4	322	1482	3641
GL 1999	2.13E+07	0.79	8.2	3.9	534	825	8.1	2.8	5.3	270	1156	2814
GL 2000	1.99E+07	0.74	8.2	3.4	496	740	8.3	2.2	5.4	274	987	2524
GL Winter	2.41E+06	0.09	1.8	0.6	112	142	1.9	0.8	0.7	94	162	516
BR 1998	6.47E+06	0.38	11	3.0	384	478	0.9	2.6	0.3	112	757	1749
BR 1999	9.64E+06	0.57	18	4.5	561	701	1.2	5.3	1.4	159	1135	2587
BR 2000	8.66E+06	0.51	15	3.8	480	611	1.0	5.0	1.3	141	1023	2281
BR Winter	2.12E+06	0.12	5.3	1.2	183	207	0.2	1.1	0.8	79	315	791

(b)

	Q (m^3)	Specific Q (m^3/m^2)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total
GL/BR 1998	6.07	3.82	1.06	1.78	1.56	2.52	12.30	0.88	17.08	2.86	1.96	2.08
GL/BR 1999	2.21	1.39	0.45	0.87	0.95	1.18	6.97	0.52	3.75	1.69	1.02	1.09
GL/BR 2000	2.30	1.45	0.54	0.90	1.03	1.21	8.66	0.45	4.02	1.94	0.96	1.11

Table 4. 5 Principal weathering reactions expected in the Bow Lake area based on catchment geology.

1.	Carbonation of carbonate: $(Ca, Mg)CO_{3(s)} + CO_{2(aq)} + H_2O \rightarrow (Ca, Mg)^{2+} + 2HCO_3^-$
2.	Pyrite oxidation: $2FeS_{2(s)} + 4H_2O + 6O_2 \rightarrow Fe_2O_{3(s)} + 4\ SO_4^{2-} + 8H^+$
3.	Pyrite oxidation couple with carbonate dissolution: $4FeS_{2(s)} + 16(Ca_{1-x}, Mg_x)CO_{3(s)} + 15\ O_{2(aq)} + 14H_2O \rightarrow$ $16\ (1-x)Ca^{2+} + 16x\ Mg^{2+} + 16HCO_3^- + 8\ SO_4^{2-} + 4\ Fe(OH)_{3(s)}$
4.	Dissolution of Anhydrite: $CaSO_{4(s)} \rightarrow Ca^{2+} + SO_4^{2-}$
5.	Carbonation of an alkali feldspar: $Na_{1-x}K_xAlSi_3O_{8(s)} + 9H_2O + 2H_2CO_3 \rightarrow AlSi_2O_5(OH)_4 +$ $2(1-x)Na^+ + 2xK+ +2HCO_3^- + 4H_4SiO_4$
6.	Carbonation of a Ca feldspar: $CaAl_2Si_2O_{8(s)} + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + 2HCO_3^- + H_2Si_2O_{8(s)}$
7.	Dissolution of Halite: $NaCl \rightarrow Na^+ + Cl^-$

Table 4.6 Mean summer solute concentrations (C in meq/L) in runoff from the Glacial and Bow River streams for 1998-2000, calculated from specific discharge and specific ion fluxes ($C_{1998} = Fs_{1998}/Qs_{1998}$).

	Q (m^3)	Specific Q (m^3/m^2)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total	Na:Cl	NO_3^-:Cl^-	SO_4^{2-}:Cl^-
GL 1998	3.93E+07	1.45	7.7	3.7	411	828	8.0	1.6	3.7	221	1019	2504	4.8	2.3	139
GL 1999	2.13E+07	0.79	10.4	4.9	678	1046	10.3	3.5	6.7	342	1466	3568	3.0	1.9	98
GL 2000	1.99E+07	0.74	11.1	4.7	672	1005	11.2	3.0	7.3	371	1339	3425	3.7	2.4	122
GL Winter	2.41E+06	0.09	19.8	7.1	1247	1590	21.7	8.7	8.1	1056	1815	5774	2.3	0.94	122
BR 1998	6.47E+06	0.38	27.7	8.0	1008	1258	2.5	6.9	0.8	296	1991	4598	4.0	0.12	43
BR 1999	9.64E+06	0.57	32.0	7.9	989	1236	2.0	9.4	2.5	281	2001	4561	3.4	0.26	30
BR 2000	8.66E+06	0.51	29.8	7.5	942	1198	1.9	9.8	2.6	277	2008	4477	3.0	0.27	28
BR Winter	2.12E+06	0.12	42.5	9.3	1465	1655	1.7	9.1	6.5	629	2521	6340	4.6	0.71	69

Table 4.7 Average solute concentrations (μeq/L) measured in winter snowpack at Bow Lake.

Site	Date	SWE (mm)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	$NO_3^-:Cl^-$
GL	02/15/99	233	2.2	1.2	3.0	8.8	0.0	1.2	3.2	2.3	11.0	2.7
BR	02/16/99	364	1.5	0.4	1.4	3.4	0.0	0.7	2.8	1.2	3.2	4.0
BR	01/29/00	180	6.0	1.0	2.6	10.7	0.0	2.9	4.8	2.3	12.5	1.7
BR	03/18/00	268	2.8	2.1	4.3	13.6	0.0	2.3	4.9	2.1	13.5	2.1
GL	03/18/00	266	3.9	4.1	4.3	12.0	0.0	2.0	5.1	2.5	16.2	2.6
Mean		262	*3.3*	*1.8*	*3.1*	*9.7*	*0.0*	*1.8*	*4.2*	*2.1*	*11.3*	2.6
SD		67	*1.7*	*1.5*	*1.2*	3.9	*0.0*	*0.9*	*1.1*	*0.5*	*4.9*	*0.9*

Table 4.8 $\delta^{34}S$ and $\delta^{18}O$ of SO_4^{2-} from stream and snow samples. $\delta^{34}S$ in in ‰ CDT, and $\delta^{18}O$ in ‰VSMOW. Mean values for Cambrian Evaporites from (Claypool et al., 1980). [SO_4^{2-}] in μeq/L.

Sample	Date	$\delta^{34}S$	$\delta^{18}O$	[SO_4^{2}]
GL	3/18/00	28.9	4.1	1213
GL	7/26/00	27.0	1.6	271
BR	3/18/00	18.9	-9.9	689
BR	7/26/00	18.1	-9.8	338
Snow	3/18/00	14.1	4.2	2.3
Cambrian evaporites		30	14	

Table 4.9 Correlation matrices for the concentrations of cations, sulphate and bicarbonate in stream water samples from (a) Bow River and (b) Glacial stream

(a)

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	SO_4^{2-}	HCO_3^-
Na^+	1.00	0.86	0.78	0.75	0.70	0.72	0.70
K^+	0.86	1.00	0.71	0.68	0.57	0.58	0.69
Mg^{2+}	0.78	0.71	1.00	0.98	0.81	0.86	0.95
Ca^{2+}	0.75	0.68	0.98	1.00	0.78	0.87	0.94
Sr^{2+}	0.70	0.57	0.81	0.78	1.00	0.92	0.63
SO_4^{2-}	0.72	0.58	0.86	0.87	0.92	1.00	0.67
HCO_3^-	0.70	0.69	0.95	0.94	0.63	0.67	1.00

(b)

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	SO_4^{2-}	HCO_3^-
Na^+	1.00	0.68	0.84	0.87	-0.04	0.43	0.85
K^+	0.68	1.00	0.77	0.76	0.26	0.51	0.73
Mg^{2+}	0.84	0.77	1.00	0.97	0.17	0.70	0.92
Ca^{2+}	0.87	0.76	0.97	1.00	0.13	0.59	0.96
Sr^{2+}	-0.04	0.26	0.17	0.13	1.00	0.44	0.02
SO_4^{2-}	0.43	0.51	0.70	0.59	0.44	1.00	0.38
HCO_3^-	0.85	0.73	0.92	0.96	0.02	0.38	1.00

Table 4.10 $^{87}Sr/^{86}Sr$ ratio and Sr^{2+} concentrations measured by ID-TIMS for the Bow River (BR) and the Glacial stream (GL). The R^2 for the linear regressions of Sr^{2+} concentrations as a function of the $^{87}Sr/^{86}Sr$ ratios are indicated.

Sample	$^{87}Sr/^{86}Sr$	+- 2sm	Sr µeq/L (ID-TIMS)	Mg^{2+}	Ca^{2+}
BR 051495 10:00	0.716453	0.000019	1.39	932	1207
BR 052698 17:45	0.715933	0.000015	1.52	884	1137
BR 061298 18:30	0.716059	0.000016	1.79	961	1186
BR 072098 10:40	0.716577	0.000018	1.95	1071	1324
BR 072798 13:00	0.716136	0.000013	1.43	896	1229
BR 081998 17:00	0.716132	0.000016	2.42	1178	1414
GL 051298 13:00	0.709972	0.000016	8.48	726	1068
GL 052698 13:30	0.710045	0.000016	7.80	566	891
GL 061398 13:10	0.710046	0.000014	9.23	537	896
GL 072898 10:00	0.710129	0.000019	6.37	415	879
GL 072898 15:00	0.710218	0.000017	4.61	427	1065
GL 081998 15:20	0.710072	0.000019	7.62	480	871

Table 4.11 NO_3^- concentrations in soil solutions collected from tension lysimeters at 4 sites around Bow Lake in 2000.

Soil Lysimeter Site	Depth	Mean $NO_3^- \pm SD$ (μeq/L)	N	Site Description
BR – S1	12 cm	1.0±1.2	10	Small willows and plant litter underlain by soil with a thin organic horizon (2-3cm), organic A horizon (5cm), and oxidized (brown-orange) B horizon
	24 cm	2.1±1.8	11	
BR – S2	12 cm	29 ± 22	10	Grassy area underlain by shallow poorly developed sandy soil (0-8 cm), sand and gravel at depth.
	24 cm	92 ± 57	10	
GL – S1	12 cm	129±53	9	Litter and humus at surface (2cm), underlain by fines/silt
	24 cm	166±57	9	
GL – S2	12 cm	0.9±0.3	4	Forested area, with grass and small plants. Soil has a thin organic horizon (4cm), leached A horizon (4cm), and oxidized (brown-orange) B horizon
	24 cm	1.0±0.5	5	

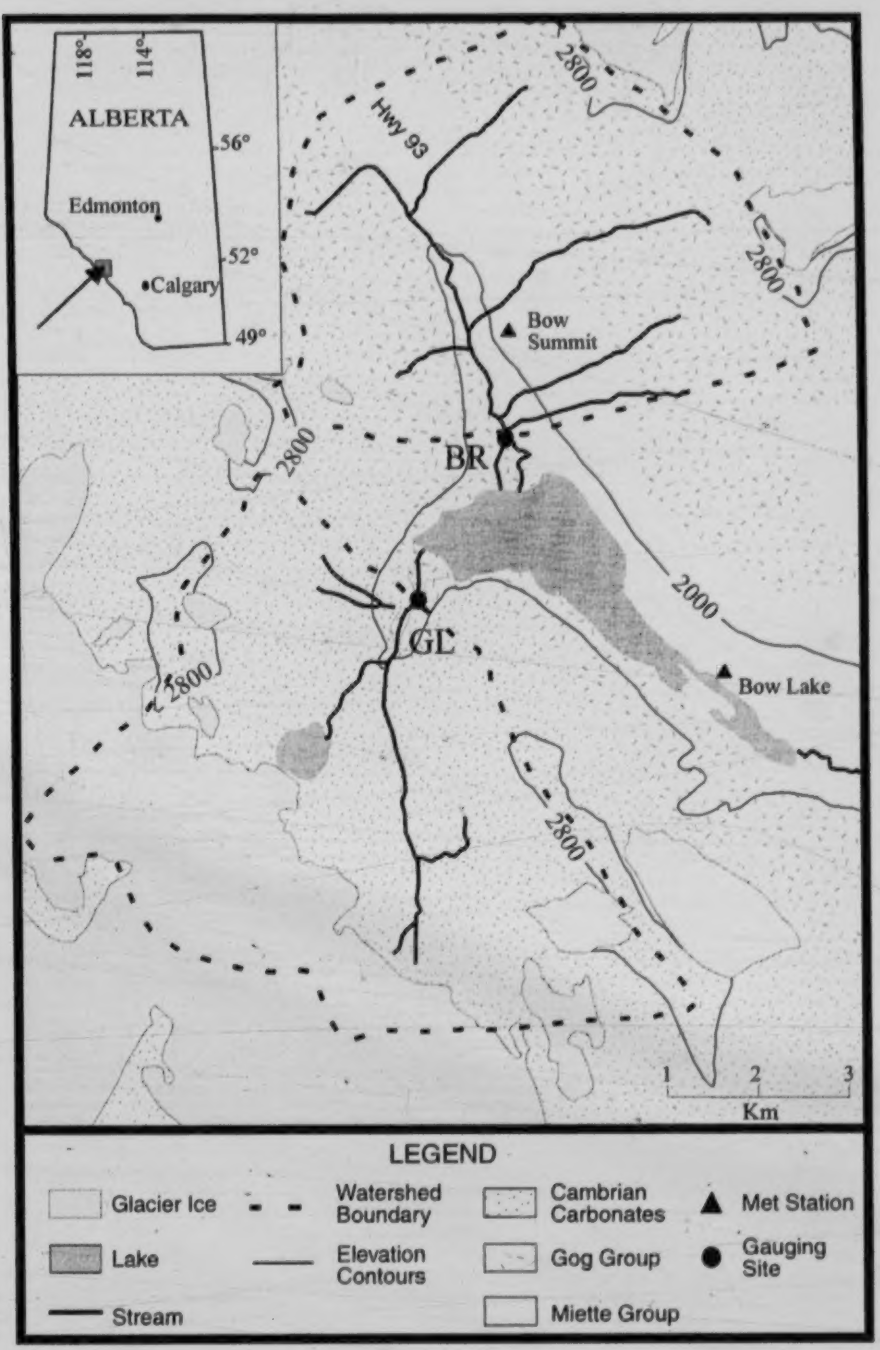
118°
114°
ALBERTA
56°
Edmonton
52°
Calgary
49°
Hwy 93
2800
2800
Bow Summit
BR
2800
2800
GL
2000
Bow Lake
2800
1
2
3
Km
LEGEND
Glacier Ice
Watershed Boundary
Cambrian Carbonates
Met Station
Lake
Elevation Contours
Gog Group
Gauging Site
Stream
Miette Group

Figure 4.1 Map of the bedrock geology and boundaries of the Bow River (BR) and Glacial stream (GL) catchments. Locations of the gauging/sampling sites for BR and GL, and of the weather stations are shown.

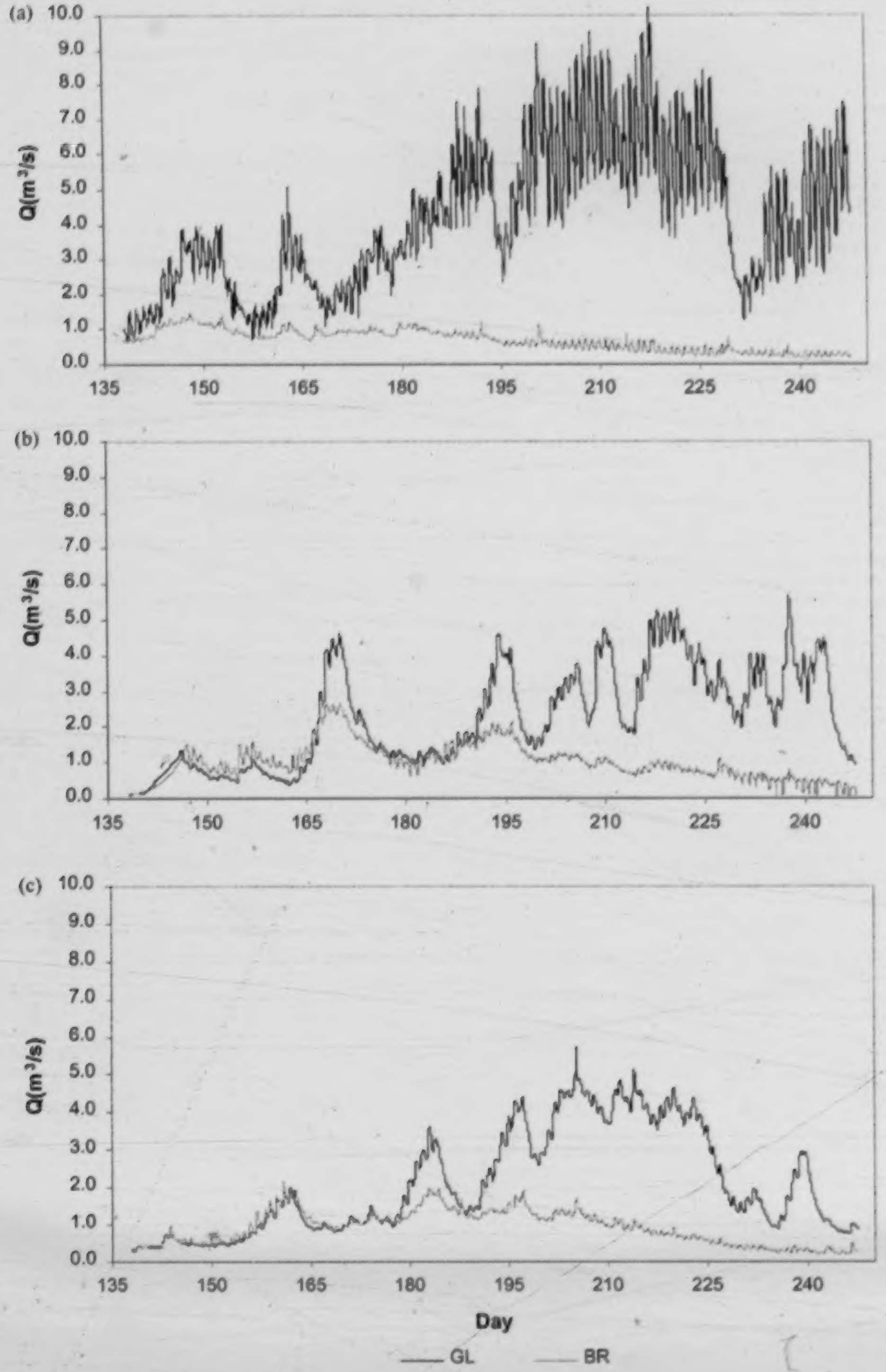

Figure 4.2 Hourly stream discharge (m^3/s) records for the Bow River and the Glacial stream for days 137-247 (May 17th to September 4th) (a) 1998, (b) 1999 and (c) 2000.

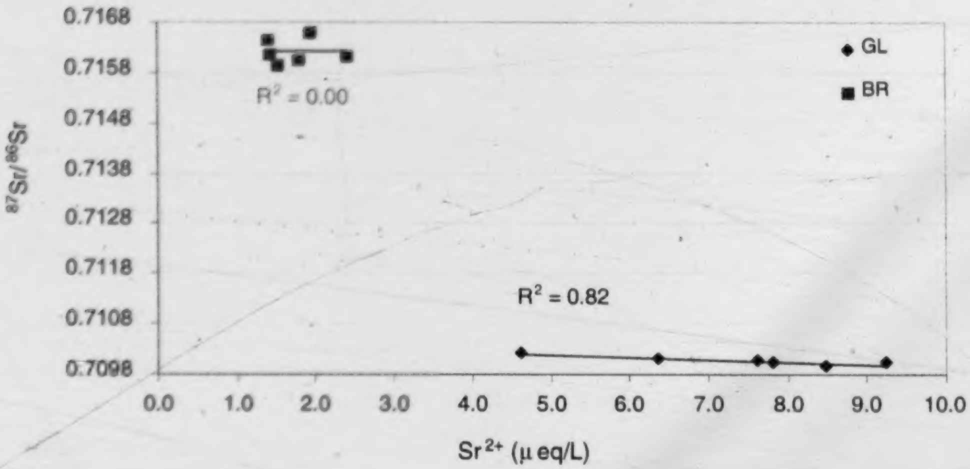

Figure 4.3 $^{87}Sr/^{86}Sr$ ratios vs. Sr^{2+} concentrations in the Glacial stream (GL) and Bow River (BR). The R^2 for the linear regressions of Sr^{2+} as a function of $^{87}Sr/^{86}Sr$ are indicated.

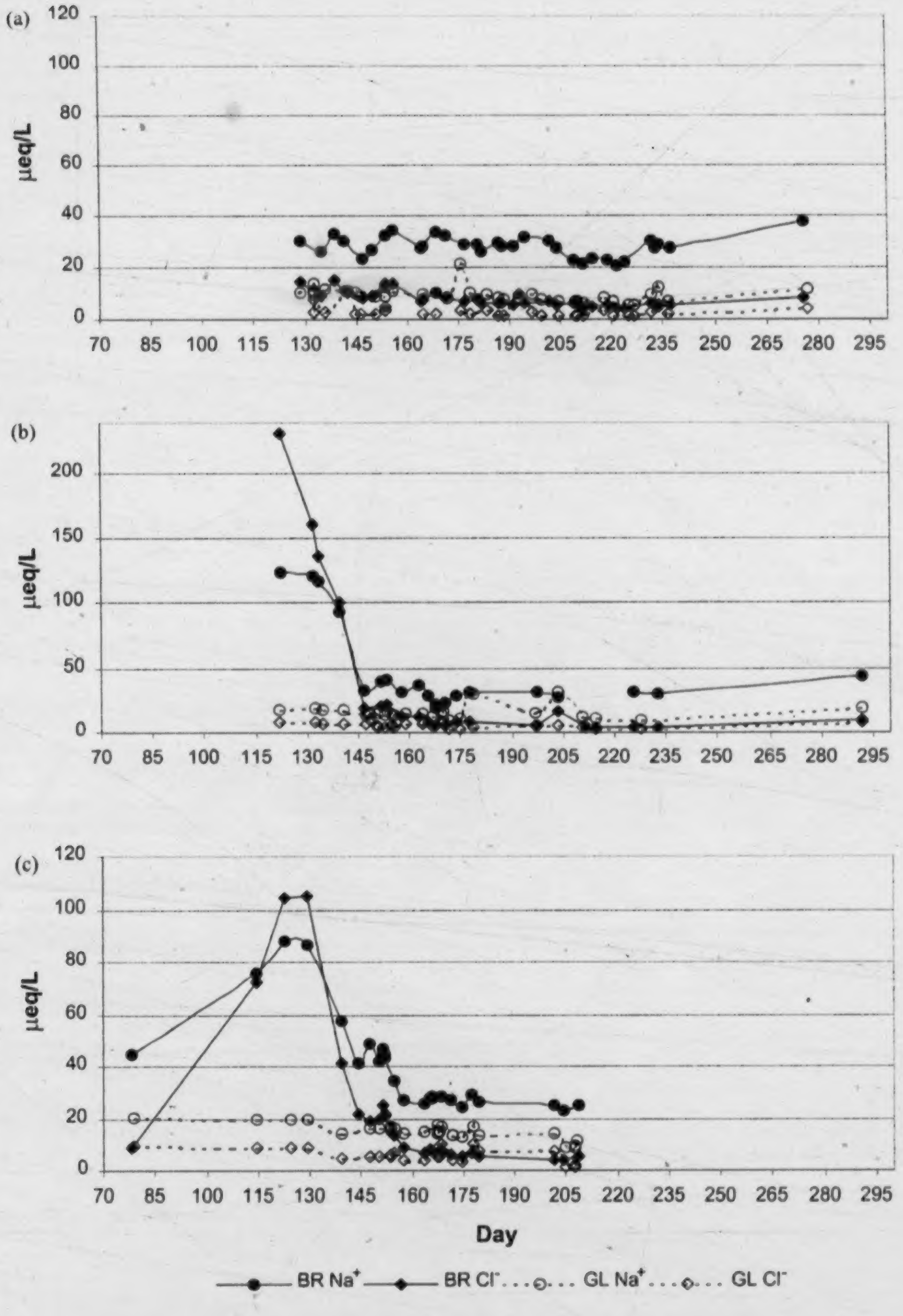

Figure 4.4 Seasonal variations in Na⁺ and Cl⁻ concentrations in the Bow River and Glacial stream (a) 1998, (b) 1999 and (c) 2000

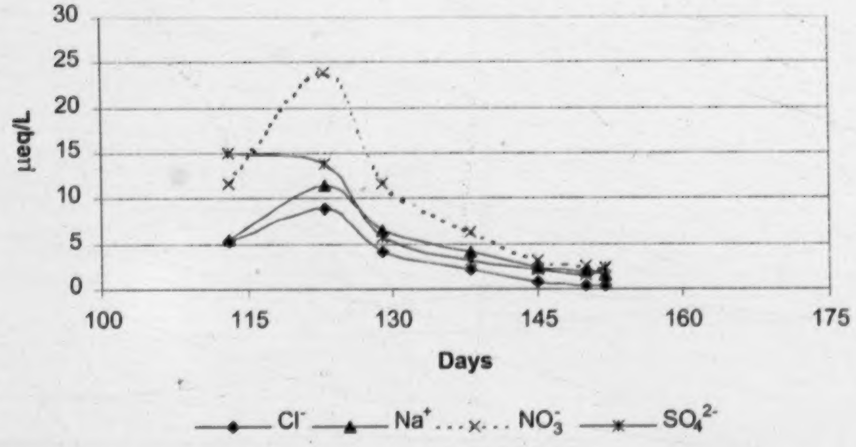

Figure 4.5 Concentrations of Na^+, Cl^-, NO_3^-, and SO_4^{2-} in meltwater collected in lysimeters at the base of the snowpack (before the ground surface) in the Bow River catchment in 2000.

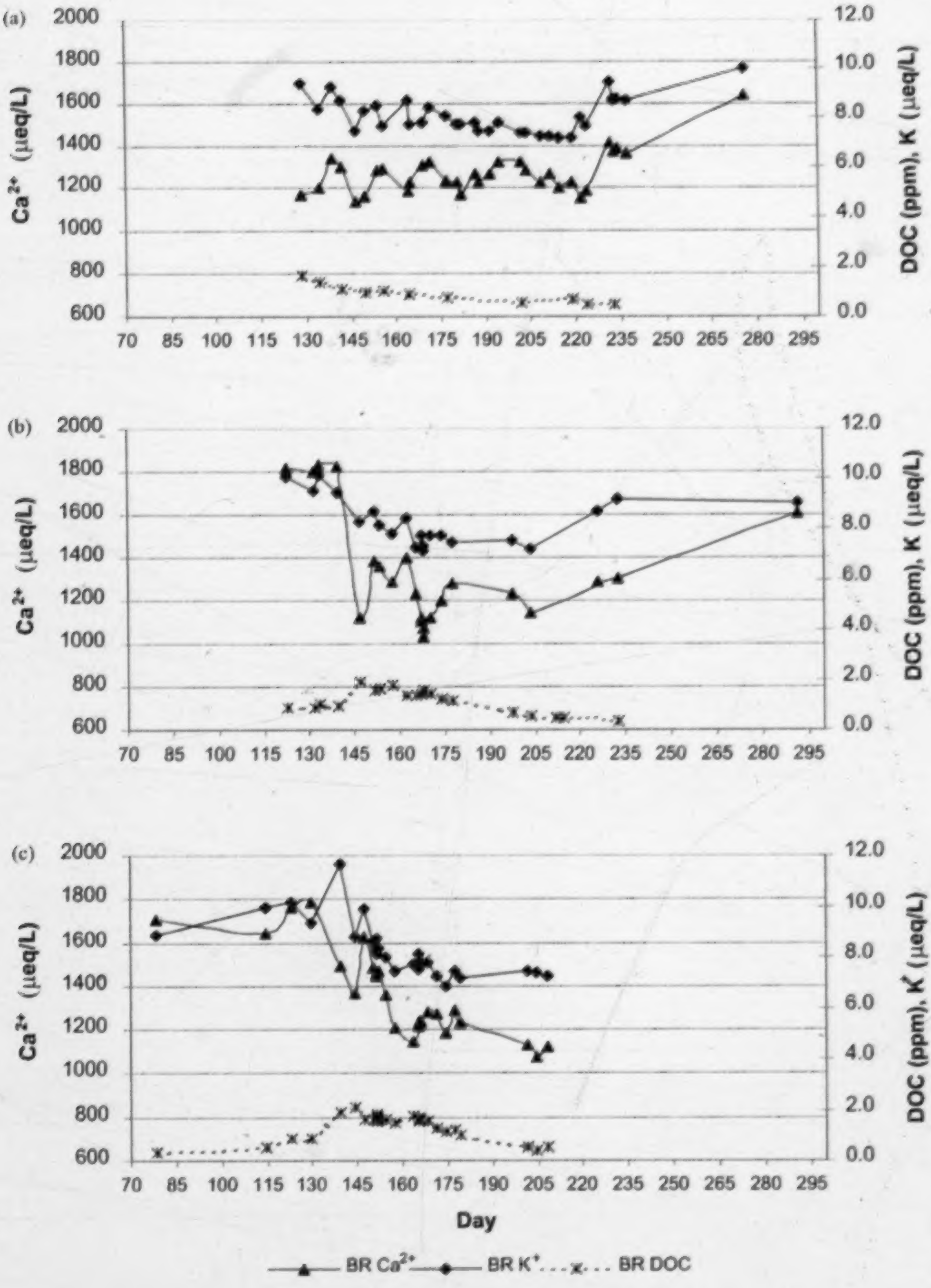

Figure 4.6 Seasonal variations in the concentrations of DOC, Ca^{2+} and K^{+} in the Bow River a) 1998, (b) 1999 and (c) 2000

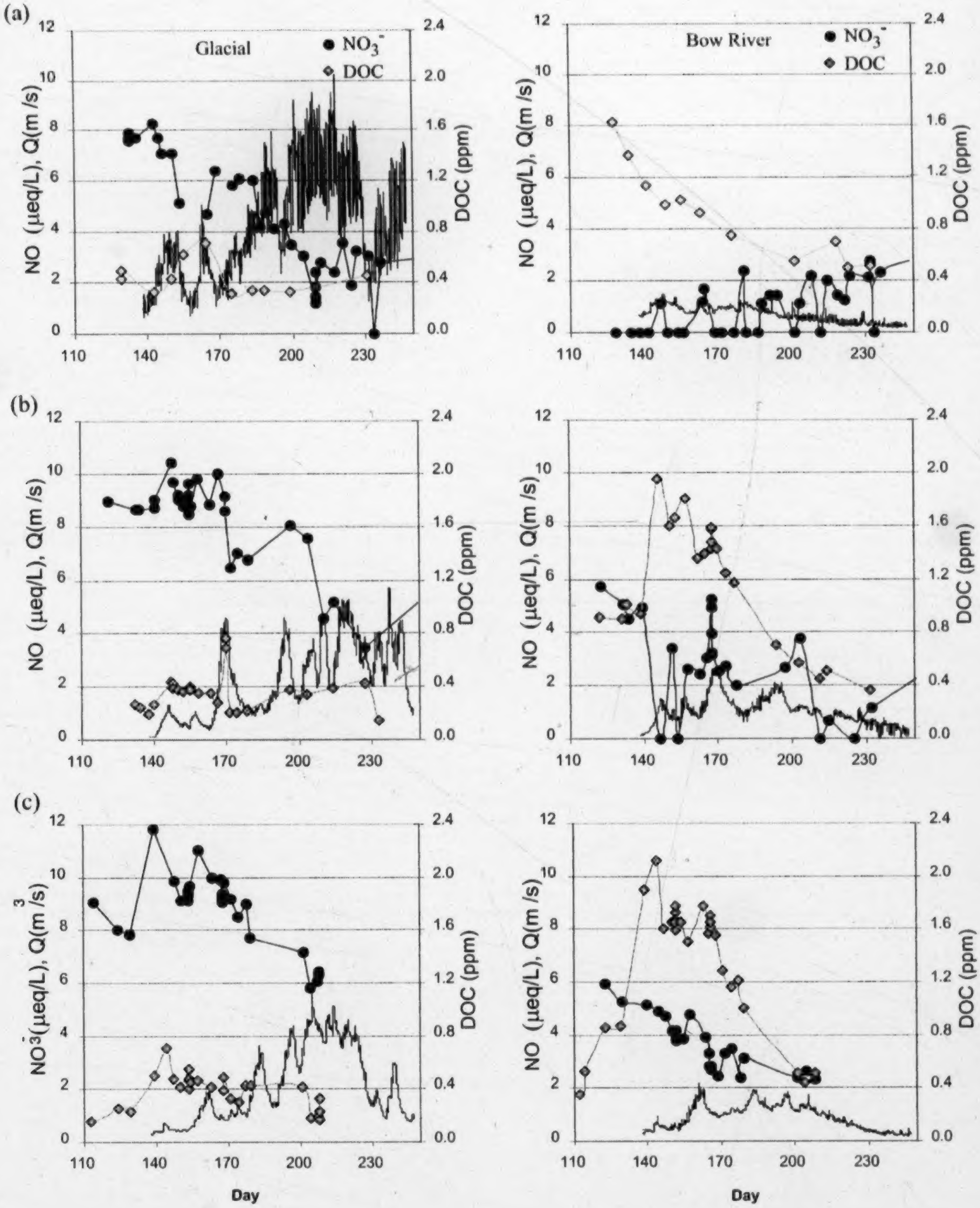

Figure 4.7 Seasonal DOC and NO $_3^-$ concentrations for the Glacial stream (left) and the Bow River (right) in a) 1998, (b) 1999 and (c) 2000

Chapter 5: Spatial and temporal variability of OC concentrations in snow, snowmelt and runoff at Bow Lake 1997-1998[1]

5.1 INTRODUCTION

Organochlorine (OC) contaminants, including polychlorinated bi-phenyls (PCBs) and organochlorine pesticides, are transported long distances in the atmosphere and deposited (primarily in snow) in many cold remote locations, including the Canadian arctic and the Canadian Rocky Mountains (Barrie et al., 1992; Blais et al., 1998; Donald et al., 1999). The deposition and accumulation of OC contaminants at high latitude and altitude are due to the effects of 'cold condensation' (Wania and Mackay, 1993). Cold condensation is the enhanced condensation and removal of organic chemicals from the atmosphere in cold regions that results from the reduction of vapour pressure with temperature, which enhances gas/particle and gas/ice partitioning (Franz and Eisenreich, 1998). In western Canada, contaminant burdens in snow were shown to increase 10 to 1000 times over an elevation range of approximately 2300 m, due to a combination of higher OC concentrations in snow at higher altitudes and increasing precipitation with altitude (Blais et al., 1998).

The properties that are key to understanding the movement of OCs in the environment include vapour pressure (P_L), aqueous solubility (C_L), the partition coefficients between organic carbon and water (K_{oc}) and/or lipids and water (K_{ow}), and the Henry's law constants, which determine the partitioning between air and water. These physical properties and the current use and status of the OCs considered in this study are listed in Table 5.1. The abundance of contaminants in the snowpack in any given year will be a function of the emissions and atmospheric abundance of contaminants in source regions, the efficiency of the transport and scavenging of contaminants from the atmosphere, and the retention of contaminants within the snowpack over the winter months (Figure 5.1). The exchange of contaminants between the atmosphere and the surface can occur by dry deposition of particles, gas exchange, and scavenging by precipitation (wet deposition). The deposition of atmospheric contaminants by snowfall can be significant because snow scavenges contaminants in the vapour phase, as well as those associated with aerosols (Franz et al., 1997). The fate and transport of OC contaminants stored in the annual snowpack are controlled by partitioning processes induced by the settling and melting of the snowpack, as well as the routing of melt water in the catchment (Figure 5.1). Contaminants in the snowpack may be removed by degradation, revolatilization and sorption to particles and vegetation within the snowpack during settling, and/or firnification (Wania, 1997; Wania et al., 1998; Wania et al., 1999). During the melt phase, contaminants leached from the snowpack can be dissolved in the liquid phase, or adsorbed to organic particles or vegetation within the snowpack. Where snow overlies ground, the fraction of OCs that drains from the snowpack with the melt water is subject to catchment retention by sorption to soils or organic matter upon infiltration. Where organic matter and vegetation are sparse, or where the ground surface is frozen or otherwise impermeable, most of the OCs in the melt should be routed to streams via surface flow, and loss by retention may be limited (Figure 5.1). Where snow overlies glacial ice, OCs in melt water are also likely to be transferred to streams with limited losses due to retention or volatilization. Therefore, following deposition, the mass of OCs that is transferred from snow covered alpine catchments to the aquatic environment via streams will depend on both the source (snow/firn/ice/ melt) and the flow routing (over land, ice or subsurface) of the melt water.

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[1] A version of this chapter will be submitted for publication. The authors will include: Melissa J. Lafrenière, Martin J. Sharp, Jules Blais, and David W. Schindler. M. Lafrenière did all the writing, interpretation, and presentation of the data and results in this chapter. The OC sampling and extractions were conducted by J. Blais. Reviews of the manuscript were provided by M. Sharp.

Much of Canada receives a significant proportion of its total annual precipitation as snow, and derives a large part of its surface waters from mountainous regions that have been shown to accumulate organic contaminants (Blais et al., 1998; Donald et al., 1999). Yet, most of the work on the composition and behaviour of organic contaminants in snow and snowmelt has been carried out in the Canadian Arctic. There have been relatively few studies on the composition and behaviour of organic contaminants in snow in the mountains or the rest of Canada (Gregor, 1990; Gregor and Gummer, 1989; Gregor et al., 1995; Hargrave et al., 1988). This study is the first to examine local and inter-annual variability in OC deposition to the snowpack, and the transfer of OCs from snow to snowmelt and stream runoff in a headwater catchment of a major drainage basin of Western Canada.

5.2 SITE DESCRIPTION

Bow Lake is located in Banff National Park, Alberta, Canada (51°40N, 116°27W). Two main catchments feed Bow Lake (Figure 5.2). The principal inflow to the lake is the Glacial stream (GL), fed primarily by meltwater from the Wapta Icefield. The catchment consists primarily of glacier ice (41%, 11 km^2), till, and moraines on which soils are absent or poorly developed (till, moraine & rock ~40%). The glacial catchment is approximately 27 km^2 (as measured from the point of gauging, 3 km away from and approximately 400m below the snout of Bow Glacier) with a mean elevation of 2560 m.a.s.l. Only 12% of the glacial catchment area is forested and/or overlain by soils with developed mineral horizons (brunisols and podsols) and some organic matter accumulation (Holland and Coen, 1982). The second, non-glacial, tributary to the lake is the Bow River (BR). This catchment has a mean elevation of 2310 m.a.s.l. and an area of approximately 17 km^2. There is less than 1.5% ice cover in this catchment, and 67% of the catchment area consists of subalpine meadow and spruce-fir forests. The remaining area is sparsely vegetated (29%) or unvegetated (2%).

Recent studies at Bow Lake indicate that, after deposition, surface runoff becomes a major route of transport of OCs to the lake, and that glacial runoff is the dominant source of most OCs to the lake (Blais et al., 2001a; Blais et al., 2001b). High dissolved concentrations of most OCs in the glacially derived stream in early June 1997 suggested that most compounds were effectively eluted from the snow (Blais et al., 2001b). Relatively high OC concentrations in this stream in late summer 1997 and again in summer of 1998 also indicated the possible contribution of OCs from glacial areas (snow, firn and/or ice) (Blais et al., 2001b).

Although it is clear that glacial runoff is the major input of OCs to Bow Lake, it is not clear how the amount of snow, the snowpack contaminant load, and the extent of snow and ice melt influence the delivery of contaminants to the aquatic ecosystem. The aim of this study is therefore to investigate the transfer of OCs from the snowpack to the glacial and non-glacial streams draining into Bow Lake. We present analyses of snow, snowmelt and stream samples collected at Bow Lake in 1997 and 1998, two contrasting hydrological years. The winter of 1996/1997 experienced much higher snowfall than 1997/1998, and the spring/summer temperatures were much lower in 1997 than in 1998 (Lafrenière and Sharp, 2003). These differences in hydroclimatological conditions resulted in lower runoff from the snowmelt fed stream, and higher runoff from the glacially fed stream in 1998 (Lafrenière and Sharp, 2003).

The paper begins with an investigation of the controls on OC abundance in the snowpack at Bow Lake. It then considers the behaviour of OCs during snowmelt, using measurements of OC concentrations in meltwater collected in snowmelt lysimeters from two different sites within the catchment (and in two different years). It concludes with an investigation of the relationship between OC concentrations in samples from one glacial and one non-glacial stream draining into the lake and winter snowpack concentrations, water sources and hydrological pathways.

5.3 SAMPLING AND ANALYTICAL METHODS

5.3.1 Snow and snowmelt sampling

Four snowmelt lysimeters were installed at two different sites (2 lysimeters at each site) in February 1997. One of the lysimeter sites was an open area in a subalpine meadow on the north side of the lake ('Open', Figure 5.2), and the other site was in a spruce-fir forest on the south side ('Forest', Figure 5.2). Melt waters from the lysimeters were collected for OC analysis twice during the melt in 1997 and once in 1998. The lysimeters consisted of a wooden base and a plexiglass collection apparatus (Figure 5.3). The base was sunk into the ground, so that the top was close to the ground level. Melt water from the overlying snowpack was directed to a plexiglass container (approx. 25L) via a plexiglass funnel, which sat inside the base (Figure 5.3). A series of square plexiglass 'retainers', designed to prevent lateral transfer of melt water, were stacked on top of the funnel as snow accumulated (Figure 5.3). Lysimeters were cleaned prior to installation by scrubbing with soap and water, then distilled water, covered in plastic until installation, and then scrubbed with snow on site. Meltwater collected in the container at the base of the lysimeter, was transferred to 18-liter air-tight aluminum cans that were pre-rinsed with acetone and hexane, and transported to the lab for extraction (as described below).

Samples of the snowpack in the vicinity of the lysimeters were collected in late March in both years (when the snowpack was approaching peak depth, and before any melt had occurred), and each time meltwater was collected from the lysimeters. In 1997, snowpack samples were also taken from 11 other sites around the lake between March 24th-March 30th (Figure 5.2). The average snow water equivalent (SWE) of the snowpack at each sampling site was determined from the weight and volume of snowpack cores collected using snow tubes (3-5 snow tube measurements were taken at each site). Snowpack samples were collected and sealed in plastic bags, and slowly melted in the lab to suppress volatilization as described in other studies (Gregor and Gummer, 1989).

5.3.2 Stream gauging and sampling

The stage of each stream was recorded using a pressure transducer and data logger (hourly averages of pressure sampled every 10 seconds). Stream discharge was determined by calibrating the pressure record with discharge measured by the velocity-area method. Errors on the discharge measurements are estimated to be ±10% (Dingman, 1993). Water samples from the Glacial stream and the Bow River were collected approximately twice monthly during the summers of 1997 and 1998. As for the snowmelt samples, stream water was collected in 18-liter air-tight aluminum cans (four per sample) that were pre-rinsed with acetone and hexane.

5.3.3 Sample extraction and organic analysis

The large volume samples were transported to the Environment Canada lab in Calgary for extraction. Samples were filtered through two pre-cleaned (muffled at 300°C for 3 hrs) 0.7 μm glass fibre filters (14.2 cm diameter) using compressed ultra high purity (UHP) nitrogen. OCs in the 70-80L of filtered water were concentrated into 250 ml of dichloromethane (DCM) using a Goulden liquid-liquid extractor (Goulden and Anthony, 1985). Field surrogates (1,3,5-tribromobenzene (TBB), 1,2,4,5–tetrabromobenzene (TTBB) and δ-hexachlorohexane (HCH)) were also extracted into the DCM to determine extraction efficiencies. These solvent samples were then sent to the Fresh Water Institute in Winnipeg for column chromatography and GC analysis, according to the procedures described below.

Lab surrogates (PCB 30, PCB 204, 1,3-dibromobenzene (DBB) and endrin ketone), and 1ml of hexane were added to the solvent samples, and concentrated by evaporation, using UHP nitrogen. The evaporated sample was then purified with Florisil column chromatography to separate OCs into 3 fractions. The first fraction (37ml of hexane) contained PCBs, α-HCH, part of γ-HCH (Lindane), HCB (hexachlorobenzene), DDE (dichlorodiphenyldichloroethylene), as well as the internal standards 1,3-DBB, 1,3,5 - TBB and 1,2,4,5-TTBB. The second fraction (38ml of an 85:15 mixture of hexane:DCM) contained most of γ-HCH, 40% α-HCH, DDD (dichlorodiphenyldichloroethane), DDT (dichlorodiphenyltrichloroethane), and the field surrogate δ-HCH. The third fraction (52ml of DCM) contained Endosulphan, Dieldrin, and the lab surrogate endrin ketone. Each fraction was evaporated to <0.2 ml, then an internal standard of Mirex was added and the sample topped up with Iso-Octane to a final volume of 200 μl. One microlitre (1μl) of each fraction was injected into a gas chromatograph (GC) equipped with a DB-5 column with He carrier at 31 cm s^{-1}, and a ^{63}Ni electron capture detector. All samples were volume corrected using the internal standard Mirex.

Blank samples were consistently clean (OC pesticides all non-detectable, some PCBs between 0.01-0.2 pg/l (mean 0.06)), thus no blank corrections were applied to the data. Table 5.2 lists the method detection limits (MDLs) as determined by replicate analysis of laboratory standards. The MDL is defined as the concentration of the blank signal (c_b) plus three times the standard deviation (SD) of the lowest detectable standard (MDL = cb+3*SD, Miller and Miller, 1988). OC concentrations reported here were not adjusted for extraction efficiencies. Recoveries for the lab surrogates suggest reasonable efficiencies for the method. The statistics for the recovery percentages for the lab surrogates are presented in Table 5.3. Both the statistics for the surrogate recoveries, and the MDLs correspond well with those reported in other studies of organic contaminants in snows (Donald et al., 1999; Gregor and Gummer, 1989). Samples with surrogate recoveries below <30%, and/or where several routinely detected contaminants were below detection limits, were excluded from the analysis (9 samples).

More than 20 chlorobenzenes and OC pesticides, and most of the PCB congeners were routinely detectable in these samples. In order to focus the content, we consider 7 of the most commonly known and abundant OC pesticides, including the sum of 4 different DDT isomers (ΣDDT = p,p-DDE + p,p-DDD, + o,p-DDT + p,p-DDT), as well as PCBs presented according to their homologue groups, and as the total PCB (ΣPCB). The octa, nona and deca-chloride homologues have been omitted from the analysis, because concentrations for these groups were rarely above the MDLs (Table 5.2).

5.3.4 Assessing the origin and hydrological flow routing of stream samples

In order to assess the influence of different water sources and hydrological pathways on the concentrations of OCs in runoff, we made a qualitative assessment of the nature of the dominant source and/or flow path of each stream sample using precipitation records, snowpack data, and the results of wavelet analysis of air temperature and discharge time series. Wavelet analysis was used to quantify the variability in the discharge (Q) and air temperature (T) series, as well as the co-variance and the phase (or lag) relationships of paired T-Q time-series, continuously in time and at different scales of response as described in Lafrenière and Sharp (2003). In glacial and snow-covered catchments, changes in water sources and in hydrological storage and transfer processes manifest themselves as changes in characteristics of the discharge hydrographs, and as changes in the relationship between the air temperature and discharge time series. The features of the wavelet spectra of the discharge hydrographs, and of the wavelet cross-spectra of air temperature and discharge series, can therefore be used to interpret and identify the dominant water sources and hydrological flow paths for each sample.

Air temperature, and precipitation were measured at an automated weather station located near the outflow of Bow Lake (Figure 5.2). Air temperature was measured using a Campbell Scientific Model 107 probe with radiation shield, and daily rainfall totals were measured using a tipping bucket rain gauge (Texas Electronics model TE525). The depth of the snowpack at the Bow Lake station in 1998 was recorded using an ultrasonic depth gauge (Campbell Scientific model UDG 01). Monthly measurements of SWE from snow courses at Bow Summit (2080 m.a.s.l., 51°42N 116°28E) and Katherine Lake (2380 m.a.s.l, 51°41N 116°23E), and hourly snow pillow records from the Sunshine Village station (2230 m.a.s.l , 51°1 N 115°55 W), were provided by Alberta Environment. The Sunshine Village snow pillow data are used in some of the analyses, because it was the nearest site to Bow Lake (approximately 70 km) for which there was a continuous (hourly) snowfall record for 1996/1997 and 1997/ 1998.

5.4 RESULTS

5.4.1 OCs in the snowpack

Thirteen snow samples were collected between March 24 and March 31st 1997. Snowpack temperature and structures were not recorded at the time of sampling. However, daily mean air temperatures at Bow Lake indicate that snowmelt should have been minimal until early April. There was only one day between January 1st and March 31st 1997 when the mean daily temperature was above zero (0.2°C), and only 5 days when the maximum air temperature for any hour was above zero. The OC loads in the snow samples were dominated by HCHs (α-HCH and γ-HCH), Endosulphans (α-Endosulphan and β-Endosulphan), and PCBs (Table 5.4). These three groups made up more than 94% of the OCs in any sample; HCHs accounted for 10-26% of the total, Endosulphans 12-20%, and the sum of all PCBs (ΣPCB) 50-80%. In 1997 and 1998, Lindane (γ-HCH) and Endosulphans were the only compounds that were still in use in North America (Table 5.1). The dominance and the concentrations of these compounds in the snows at Bow Lake are generally consistent with other studies of snow and ice in western Canada (Blais et al., 1998; Donald et al., 1999).

The concentrations of contaminants varied considerably between sites across the catchment (Table 5.4). The coefficients of variation (CV = Mean/SD*100) were usually between about 25-65%, but CVs for some compounds reached 90-208% (Table 5.4). The concentrations of several contaminants, α-HCH, γ-HCH, HCB, and ΣPCB were strongly correlated ($p<0.05$) with snowpack SWE (Table 5.5). Thus, the variability between sites is greater when considering the contaminant load (ng/m^2) of the snowpack (Figure 5.4). The only notable spatial trend was that sites with lower snow accumulation and lower contaminant concentrations appeared to be primarily from forested areas within the catchment (sites 7, 8, 10, 11, 12, 13 and Forest, Figure

5.2), while the snows with higher accumulation and concentrations were generally from open, or sparsely vegetated sites (sites 3, 4, 5, 6, 14, Open, Figure 5.2).

When samples were grouped according to whether the site was primarily forested or open (Table 5.6), the average concentrations of α-HCH, γ-HCH, HCB, Dieldrin, α-Endosulphan, β-Endosulphan, and ΣPCBs were lower for forested sites ($p<0.05$). Both the SWE and density of the snowpack were also significantly lower for snow collected at forested sites than in snow from open sites (Table 5.6). The largest and most significant differences between the forested and open sites were for α-HCH (%Δ 89, $p<10^{-11}$) and γ-HCH (%Δ78, $p<10^{-10}$), α-Endosulphan (%Δ 78, $p<0.002$) and HCB (%Δ 78, $p<0.003$) (Table 5.6). Included in Table 5.6 are some ratios of more volatile compounds to less volatile OCs: α-HCH/γ-HCH, HCB/Dieldrin, β-Endosulphan/α-Endosulphan, and of (α-HCH+γ-HCH)/ΣPCB. The ratios α-HCH/γ-HCH, HCB/Dieldrin, and (α-HCH+γ-HCH)/ΣPCB were all significantly lower in the forested sites than in the vegetation free sites. Thus, in addition to differences in OC abundance, there appear to be differences in the composition of OC in snow samples from forested and open sites. Sites with lower accumulation and concentrations contained lower amounts of the more volatile compounds (Table 5.6).

In 1998, three snowpack samples (replicates) were collected at each lysimeter site at the end of March (Table 5.7). The snowpack temperature was not measured, however the mean monthly air temperatures recorded at the Bow Lake weather station in February (-10 °C) and in March (-8.4°C) indicate that there should have been minimal melting in the snowpack. There were only 5 days between January and the end of March when any hourly mean air temperatures were above zero (highest temp 3.5°C). The differences in concentrations between the replicates are the result of a combination of analytical variation and sampling variability. The variations in contaminant concentrations between the 3 replicate samples were generally lower than the variability in OC concentrations between the 6 samples from the two sites in 1998 (Table 5.7, mean CV = 57±33%), and lower than the variability in the concentrations between the 13 different sites in 1997 (Table 5.4, mean CV = 67±47%). For the samples taken from the Open site, the CVs for the 3 samples were between 7-52% (except for ΣDDT: CV of 91%), with an average of 30% for all compounds (Table 5.7). The variability in the OC concentrations for the replicate samples from the Forest site (CVs between 8-107%, with an average of 59%) was substantially higher than for the replicates from the Open site. However, the variability in the replicates from the Forest site appears to be primarily due to the high Dieldrin, Endosulphan, and PCB concentrations in the Forest A sample (Table 5.7). Contrary to 1997, there was little difference in the snowpack concentrations between the Open site and the Forest site in 1998. For some OCs the concentrations were higher at the Forest site (α-HCH, γ-HCH, and α-Endosulphan, $p<0.05$) than at the Open site in 1998 (Table 5.7). Only the PCBs displayed significantly higher concentrations at the Open site than at the Forest site in 1998.

On average, the OC content in the snowpack at Bow Lake was substantially lower in 1998 than in 1997 (Table 5.8). Despite the variability in snowpack concentrations in each year, the mean concentrations of α-HCH, γ-HCH, HCB, Dieldrin, α-Endosulphan, β-Endosulphan, ΣDDT, and ΣPCBs were all significantly lower (z-test, $p\leq0.003$) in 1998 than in 1997. There was also a small decrease in the snowpack height between the two years (Table 5.8), thus the differences in contaminant load in the snowpack from year to year were even greater than the differences in concentrations.

5.4.2 Contaminants in snowmelt

In 1997, snowmelt was collected from the 4 lysimeters (F1, F2, Op1, Op2) on 2 occasions, once between May 3rd and 5th, and again between May 16-17th (Table 5.9a). Due to structural problems with the lysimeters at the Open site in 1998, melt waters were only retrieved from the 2 Forest site lysimeters (F1, F2, Table 5.9b). Also, as a result of the early snowmelt in 1998, only one melt sample was collected from each of the forest lysimeters on May 9th. In 1997, the contaminant concentrations were very high in the first melt water samples collected near the beginning of May (Table 5.9a). The melt water concentrations of α-HCH, γ-HCH, α-Endosulphan, and β-Endosulphan, were usually an order of magnitude lower in the samples collected in mid-May (Table 5.9a).

The enrichment (or depletion) of contaminant concentrations in the snowmelt samples relative to the average winter snowpack concentrations is shown in Figure 5.6. The enrichment (or depletion) was calculated as the difference between the concentration of a contaminant in snowmelt ([Melt]) and the mean concentration of the contaminant in the snowpack $[\text{Snow}]_{\text{mean}}$ at the end of winter (end of March), divided by the mean concentration of the contaminant in the snow (i.e. $([\text{Melt}]-[\text{Snow}]_{\text{mean}})/[\text{Snow}]_{\text{mean}})$). This enrichment or depletion results from the combined effects of deposition between the time of last snowpack sampling and the time of snowmelt collection, and OC loss due to volatilization and adsorption to organic particles in the snowpack during melt. In addition, the enrichment factors will reflect the preferential flush and concentration of solutes in the early part of the snowmelt (Schöndorf and Herrmann, 1987).

Preferential elution leads to the release of the most soluble OC compounds (e.g. HCHs) in the first fraction of the snowmelt. The more hydrophobic compounds (e.g. PCBs, which are usually sorbed to particles) are released at the end of snowmelt (Schöndorf and Herrmann, 1987; Simmleit et al., 1986; Wania, 1997; Wania et al., 1999). If a compound is enriched in the melt relative to the end of March snowpack, this therefore indicates that the combination of deposition and elution processes exceeded any losses due to volatilization or particle adsorption during snowmelt. Since the variability of contaminants in the snowpack was relatively high (Table 5.4 and 5.7), the significance of the enrichment/depletion factors for the contaminants is evaluated and discussed. The difference between the contaminant concentration in melt and snowpack was considered significant if it was greater than the standard deviation of the mean snowpack concentrations (i.e. $(([\text{Melt}]-[\text{Snow}]_{mean})/\text{SD of }[\text{Snow}]_{mean}) > \pm 1$).

The first snowmelt samples in 1997 exhibited strong enrichment for most OC pesticides (Figure 5.6a) and some PCBs (Figure 5.6b), while the second melt samples in 1997 were depleted of most contaminants relative to the March snowpack (Figure 5.6a and 5.6b). The most soluble, and less hydrophobic HCHs experienced the most enrichment, followed by the Endosulphans, which also have relatively high aqueous solubility and low hydrophobicity (see Table 5.1 for solubility and K_{ow} values). The HCHs were enriched in the first snowmelt samples at all four lysimeters in 1997, and again in the two samples from the forest lysimeters in 1998. The snowmelt concentrations were approximately 5-16 times the mean snowpack concentrations for α-HCH, and 2-8 times the mean snowpack concentrations for γ-HCH (Figure 5.6a). The enrichment of HCHs was always significant ($[\text{Melt}]-[\text{Snow}]_{mean} > 5\text{x SD of }[\text{Snow}]_{mean}$). Three out of four melt samples from 1997 were also strongly enriched in α-Endosulphan and β-Endosulphan. The enrichments were approximately 1 to 3 times the mean concentrations in snow for α-Endosulphan, and 2 to 5 times the mean snow concentrations for β-Endosulphan (Figure 5.6a). The enrichment factors for the Endosulphans were all significant. Although the melt sample from the first Forest lysimeter (F1 06/05/97) was depleted in Endosulphans relative to the average concentration of all the snowpack samples in the catchment, the Endosulphan concentrations in the F1 06/05/97 melt were actually higher than those in the snowpack adjacent to the lysimeters at this site (compare F1 06/05/97 in Table 5.9a with Forest snow in Table 5.4).

The more hydrophobic Dieldrin and HCB were a lot less concentrated in the snows than the more soluble HCHs and Endosulphans, and they displayed smaller and less frequent enrichment in the snowmelt samples. Dieldrin was slightly, but significantly, enriched in the

1997 melts (0.6-2.1 times $[\mathrm{Snow}]_{\mathrm{mean}}$), while HCB was only enriched in the Op2 03/05/97 and F2 09/05/98 samples. The apparent depletion of Dieldrin in the 1998 melt samples, may be due to the very high Dieldrin concentration (48.7 pg/L) found in the Forest site 03/25a snow sample, which led to a high average concentration and large SD for Dieldrin in the 1998 snowpack (Table 5.5). Where HCB was enriched, the enrichment was only 1-1.2 times the SD of the HCB concentration in the snowpack, and thus only marginally significant. ΣDDT showed a different behaviour in the snowmelt from year to year (Figure 5.6a). In 1997 ΣDDT was always slightly depleted in the snowmelt, but in 1998 ΣDDT was strongly (1.8 and 4.9 x $[\mathrm{Snow}]_{\mathrm{mean}}$) and significantly enriched in both melt samples (Figure 5.6a).

The enrichment of PCBs in the snowmelt was less consistent across sites than for most of the OC pesticides. In the early May melt samples from both 1997 and 1998, one sample from each site showed strong and significant enrichment in most PCBs (F1 06/05/97, Op2 03/05/97, and F2 09/05/98). The other was primarily depleted in PCBs relative to the snowpack (Figure 5.6b). When the ΣPCB concentrations in the melts were depleted or approximately equal to the snowpack concentrations, however, the heavier (less volatile, more hydrophobic) penta, hexa, and hepta-chloro homologue groups were usually slightly (and sometimes highly) enriched in the melt water (Figure 5.6b).

5.4.3 OC concentrations in streams 1997-1998

The Bow River and Glacial streams were both sampled on seven occasions during the spring and summer of 1997 and 1998 (Table 5.10). In 1997 the OC concentrations in runoff were highest in early June. In 1998 the late July and August samples had the highest OC concentrations (Table 5.10). The mean contaminant concentrations in each stream were generally higher in 1997 than in 1998. The inter-annual differences in the OC concentrations in the streams were, however, much smaller than the inter-annual differences observed in the snow and snowmelt samples (Tables 5.8 and 5.9). The mean concentrations of the OC pesticides were usually higher in the Glacial stream than in the Bow River (Table 5.10). HCB and the PCBs were the only contaminants for which the mean concentrations in the two streams were not significantly different (z-test, $p<0.05$), and ΣDDT was the only contaminant for which the mean concentrations were higher on average in 1998 than 1997 (z-test, $p<0.004$).

As with the snowmelt samples, the OC concentrations in each stream sample were compared to the mean OC concentrations in the snowpack at the end of March of the preceding winter: ([Stream]-[Snow]mean)/[Snow]mean. These results are shown in Figures 5.7 and 5.8. The significance of the enrichment/depletion was evaluated in the same way as for snowmelt: $(([Stream]-[Snow]_{mean})/SD$ of $[Snow]_{mean}) > \pm 1)$. As for the snowmelt samples, the enrichment or depletion potentially reflects the addition of contaminants as a result of deposition after the time of last snowpack sampling, the loss of OCs due to volatilization and adsorption to organic particles in the snowpack during melt, and the preferential elution and concentration of OCs during snowmelt. The enrichment of the contaminants in the stream is likely to be lower than was observed for the first snowmelt fractions, since stream runoff averages meltwater inputs from the snowpack, which will be at different stages of melting in different areas in the catchment. There is also the potential for additional contaminant losses by sorption to organic matter and volatilization during the routing of snowmelt to the stream. Melt inputs from glacier ice can also represent an additional source of OCs that could potentially enhance the stream water enrichment relative to snowpack. The enrichment of a contaminant in the stream relative to the snow therefore indicates that there was minimal loss of contaminants during the transfer of the meltwater to the channel.

In 1997, the only stream sample that displayed any enrichment in OCs with respect to the average March snowpack concentrations was the June 7th sample (day 158) from the Glacial stream (Figure 5.7a). In this sample, α-HCH, γ-HCH, and the penta-chloro and hexa-chloro PCBs were all significantly enriched in the stream. The di-chloro and hepta-chloro PCBs were also slightly enriched, but the enrichments were not significant. The Endosulphans, which exhibited relatively strong enrichments in the meltwater, were always depleted in the stream waters. For all the other 1997 samples, the OCs were either depleted or not significantly different from the snowpack concentrations (Figure 5.7).

In 1998 the stream waters displayed higher and more frequent enrichment in OCs than in 1997 (Figure 5.7 and 5.8). In the Glacial stream, all samples, except for May 18th, were strongly and significantly enriched in α-HCH, γ-HCH, and ΣDDT (Figure 5.8a(ii)). Dieldrin and HCB were also usually enriched in the Glacial stream samples in 1998, but the enrichments for these contaminants were small, and not always significant. ΣDDT was very strongly enriched in the Glacial stream in the June 7th sample, and then again in the July 27th and August samples. The hexa and hepta-chloro PCBs were slightly, but significantly, enriched in the May 9th and June 7th samples (Figure 5.8 a(ii)). The mono-chloro PCBs appear to be enriched in some samples, however, the enrichments are not considered significant because of the very high variability in the concentration of this homologue group in the snowpack (Table 5.7).

Enrichments in OCs were much lower and less frequent in samples from the Bow River. The concentrations of most pesticides in the May 8th 1998 sample from the Bow River were very similar to, or slightly lower, than the March snowpack concentrations, with the exception of γ-HCH, which was significantly enriched (Figure 5.8b(i)). The Bow River was also significantly enriched in several OC compounds on July 26th (α-HCH, HCB, Dieldrin and ΣDDT) and August 9th (α-HCH, γ-HCH, HCB, and ΣDDT). ΣDDT was also significantly enriched in the Bow River on June 6th and June 22nd (Figure 5.8b(i)). The trends in PCBs concentrations in the Bow River, were very similar those for the Glacial stream in 1998 (Table 5.10). As with the Glacial stream, the May 8th sample in the Bow River was the least depleted in PCBs of all samples, and the hexa and hepta-chloro PCBs were significantly enriched (Figure 5.8b(ii)). The hepta-chloro PCBs were enriched again in the June 6th sample from the Bow River.

5.4.4 Dominant water source(s) and flow path(s) of stream water samples

The daily average discharge and total daily precipitation records for the 1997 and 1998 seasons are plotted in Figures 5.7c and 5.8c, respectively, along with the times of sampling. Tables 5.11 and 5.12 present the rainfall and snowpack data, as well as the main features of the discharge hydrographs, and results of the wavelet analysis. The following section discusses how these data were used to determine the dominant water sources and hydrologic pathways listed in the tables.

The retreat of the seasonal snowpack in an ice-free catchment should result in a decrease in the amplitude of the diurnal discharge signal, a decrease in the responsiveness of discharge to longer scale (4-8 day) temperature variability, and a recession of the discharge hydrograph (Lafrenière and Sharp, 2003). Therefore, in an ice-free catchment the retreat of the snowpack should be indicated by a decrease in the variance (or power) in the discharge wavelet spectrum at 24-hour ($W_n^{QQ}(24hr)$) and longer timescales ($W_n^{QQ}(>96hr)$), and mean daily discharge values below the seasonal mean (i.e. $(Q_d\text{-}Q_s)/Q_s<1$). Since the exposure of glacier ice amplifies the response of discharge to temperature variations, this event should be marked by a significant increase in the daily mean discharge, and increases in the power in the discharge wavelet spectrum at diurnal ($W_n^{QQ}(24hr)$) and longer timescales ($W_n^{QQ}(>96hr)$ (Lafrenière and Sharp, 2003). The development of major channels in the glacier system may also lead to further increases in the variance in the wavelet spectrum of discharge at 24-hour and shorter timescales ($W_n^{QQ}(<24hr)$) and possibly a decrease in the phase (or lag) between temperature-discharge signals at the 24 hour scale ($\theta^{TQ}(24hr)$). Discharge response to rainfall is also indicated by sudden changes in $\theta^{TQ}(24hr)$. It is also shown by the presence of significant variance in the wavelet power spectrum for discharge that is not associated with significant co-variance in the temperature-discharge wavelet cross-spectra (*Strong* $W_n^{QQ}(s)$, *No Strong* $W_n^{TQ}(s)$). This implies that the discharge variability is not due to temperature induced meltwater runoff, but to a non-melt water source such as rainfall.

In 1997, the major snowmelt event occurred between June 9th and June 24th (day 160-175). This event is marked by very strong $W_n^{QQ}(24hr)$ power in both streams (Table 5.11). By the end of June (after day 180), the $W_n^{QQ}(24hr)$ and $W_n^{QQ}(>96hr)$ in both streams decrease dramatically, and the mean daily discharge values fall below the seasonal mean (i.e. $(Q_d-Q_s)/Q_s<1$), indicating that most snow in the catchments had retreated by this time. This inference is supported by the snow pillow data from Sunshine Village, which recorded that the snowpack there was gone by July 7th (Table 5.11). The moderate increase in the $W_n^{QQ}(24hr)$ and $W_n^{QQ}(>96hr)$ power for the Glacial stream discharge, and similar but weaker increase for the Bow River discharge, around July 14th (day 195) indicates that meltwater from ice covered areas likely contributed slightly to runoff in both streams by mid July (Lafrenière and Sharp, 2003). The lack of any high frequency power in the wavelet spectra for discharge, (i.e. $W_n^{QQ}(<24hr)$), and the absence of any seasonal change in the phase relationship between temperature and discharge suggests that there was little development of the subglacial drainage system in 1997 (Lafrenière and Sharp, 2003).

In 1998, snow at the Bow Summit weather station had melted by May 30th, and less than 30 mm SWE remained at the Sunshine Village snow pillow site on June 1st (Table 5.12). The wavelet analyses of the discharge hydrographs show that, with the exception of some short lived diurnal power between approximately June 11th and 15th (day 162-166), there was little variability in runoff until approximately July 9th (after day 190), and hence little snowmelt in either catchment. Sometime around mid July (day 190-195) the power for $W_n^{QQ}(24hr)$ increases to significant levels in both streams (Lafrenière and Sharp, 2003). The dramatic increase in the daily mean discharge ($(Q_d-Q_s)/Q_s<1$) and the $W_n^{QQ}(>96hr)$ in the Glacial stream by mid July indicate that glacially derived meltwater was contributing significantly to runoff by this time (Table 5.12). The significant and persistent diurnal (i.e. $W_n^{QQ}(24hr)$) and higher frequency power ($W_n^{QQ}(<24hr)$) in the Glacial stream discharge during the month of August (days 215-245) strongly suggests that there was likely development of subglacial channels in late summer 1998 (Table 5.12). The shift in the phase lag ($\theta^{TQ}(24hr)$) from approximately 7 h to 4.5 h around day 190 in 1998 is also an indication of the exposure of glacial ice and/or the development of subglacial channels (Lafrenière and Sharp, 2003). The persistent diurnal scale power in the Bow River throughout the summer in 1998 also indicates late summer melt input from an ice or firn/snow source in this catchment (Lafrenière and Sharp, 2003).

5.5 DISCUSSION

5.5.1 Spatial and temporal variability in OCs in the snowpack 1997-1998

5.5.1.1 Replicate samples

The variability in the replicates from the Open site (CVs 7-52%, mean=30%) is consistent with that reported for the same contaminants in triplicate snow samples taken from sites in the Canadian Arctic (Gregor and Gummer, 1989) and in the Canadian Rocky Mountains (Donald et al., 1999). The variability in OC concentrations in the replicates from the Forest site was much higher for some contaminants. However, if the results for Dieldrin, Endosulphan, and PCBs in the Forest A sample are excluded (Table 5.7), the variability for contaminants in the Forest site replicates (CVs between 8-45%, mean of 36%) is similar to that observed for the Open site. Yet, besides the higher concentrations for some contaminants there is no obvious technical reason to exclude the Forest A sample from the analysis. The surrogate recoveries for the Forest A sample were virtually identical to those for Forest B sample, so it seems unlikely that there was an analytical problem with this particular sample.

It is difficult to imagine that the OC concentrations of these contaminants were so different between samples collected within metres of each other. However, if the temperature regime, physical structure, and organic matter content within the snowpack vary substantially over relatively small distances in forested environments, this could alter the partitioning processes and lead to a high degree of variability in OC concentrations over very small spatial scales. For example, less particulate organic matter in the snow, or a localized difference in the physical structure of the snow could reduce volatilization and/or removal of OCs by particle adsorption. We do not have adequate data about the nature of the snowpack at each sample site to establish whether any of these processes may explain the variability observed at the Forest site in 1998. Nevertheless, the high degree of variability observed in our replicate samples suggests that, ideally, studies of OC contamination in snow should include a careful description of the physical structure of the snowpack and measurements of the DOC/POC content for each sample. Multiple samples would also impart greater confidence to results, especially for studies in forested areas. Forests are known to be effective filters of gaseous and particle bound OCs in the atmosphere, and forest litter is an effective vector for transferring OCs to the forest soil (Davidson et al., 2003; McLachlan and Horstmann, 1998; Wania and McLachlan, 2001). Therefore, forest litter might also be a source of OCs to the snowpack, and hence might explain some of the variability observed in the snow collected from forested sites. However, we are unaware of any studies that have examined the partitioning of OCs between forest litter and the snowpack.

5.5.1.2 Catchment scale variability

The variability of the OC concentrations observed in the snows in the catchment in 1997, seems to be related to the net accumulation of snow, and/or the presence of vegetation (Table 5.6). The significantly lower SWE, OC concentrations, and ratios of α-HCH/γ-HCH, HCB/Dieldrin, in the 'forested' vs. 'open' sites indicate that the presence of vegetation resulted in lower accumulation and lower relative abundances of the more volatile compounds in the snowpack (Table 5.6).

It is well known that forest intercepts snow and increases sublimation losses due to the high surface area to volume ratio of intercepted snow (Pomeroy and Gray, 1995). It is, therefore, likely that the interception of snow by forest vegetation reduces the accumulation of contaminants on the ground and increases volatilization losses within the canopy. Also, since forests are effective at removing certain contaminants from the atmosphere by gaseous adsorption through the cuticles of needles in coniferous forests (Wania and McLachlan, 2001), forest vegetation might also reduce the concentration of OCs in snow deposited on the ground, by reducing the abundance of gaseous contaminants that are available for scavenging by falling snow. Furthermore, lower rates of accumulation at forest sites could enhance the volatilization of gaseous OCs from the within the snowpack, since the potential for diffusive or evaporative losses should increase if the contaminants are found nearer the surface of the snowpack. Studies at Amituk Lake in the Canadian Arctic, found that deeper snow retained its burden of more volatile OCs better than shallow snow (Macdonald et al., 2000).

Our data do not enable us to identify the process responsible for the observed differences in the OC loads of open and forested sites in 1997. They do, however, suggest that the extent of forests may be an important control on the accumulation of OCs in alpine environments, and therefore might contribute to the observed increase in contaminant deposition with elevation

(Blais et al., 1998). Although the observed differences in OC concentrations between the forested and open sites in 1997 were not apparent in the 1998 samples, this may reflect the smaller differences in SWE between the two sites, and lower overall OC concentrations in 1998. Therefore, it is difficult to assess the significance of the 1998 results, especially since only two sites were sampled in 1998 (compared to 13 in 1997).

5.5.1.3 Inter-annual differences in 1997 and 1998 snowpack burdens

The abundance of contaminants found in the snowpack in any given year will be a function of various factors. These include their abundance in the atmosphere in source regions, the efficiency of transport to the study site and of scavenging from the atmosphere, and the retention of contaminants within the snowpack over the course of the winter months.

Changes in the abundance of contaminants in the atmosphere will depend primarily on changes in the use, production and/or re-emission of contaminants to the atmosphere in source regions. The linkage between pesticide usage and air concentrations is clearly illustrated by the similarity in the trends in global usage and atmospheric concentrations of HCHs in the arctic regions (Li et al., 1998). Daily 5-day air mass back trajectories (HYSPLIT, NOAA, 2003) indicate that air masses arriving at Bow Lake between December and January 1996/1997 and 1997/1998 originated primarily from the south western United States and Mexico (south of 45°N and 120-130°W), and from the south west Pacific (south of 45°N, and west of 130° W). The primary source regions for contaminants deposited in snow at Bow Lake are therefore likely the west coast of the United States, Mexico, and Asia. Information on annual use, production and emissions of pesticides and PCBs is scarce. It does not, however, appear that there were any significant changes in the regulation, use, or emissions of any of the compounds considered in this study in the major source regions between 1996 and 1998 (Li, 1999a; Li et al., 2001a; Li et al., 2001b; UNEP, 2002a; UNEP, 2002b; UNEP, 2002c; UNEP, 2002d). We do not, therefore, expect that changes in use or emissions patterns between 1996/1997 and 1997/1998 could account for the 40-90% decrease in snowpack OC concentrations between March 1997 and March 1998 (Table 5.8).

The scavenging efficiency is the amount of air that is scavenged of chemical by a given volume of snow (in SWE). Many factors, such as the concentration of chemical in the air (gaseous and particle bound), air temperature, and size and shape of the snow flakes control the scavenging of contaminants from the atmosphere (Franz et al., 1997; Wania et al., 1998).

Scavenging efficiency has been observed to vary within the course of one wet deposition event, as well as between events (Franz and Eisenreich, 1998). Little is known about the scavenging of OCs by snow, or the concentration and variability of OCs in the air during the winter months in the Rocky Mountains. Studies in the Yukon and the Arctic indicate that the concentrations of most OCs in the atmosphere decrease with decreasing temperatures over the year. Rare instances of unusually high air concentrations of HCH and DDT have, however, been observed during the winter as a result of trans-Pacific transport from east Asia (Bailey et al., 2000; Halsall et al., 1998). Our lack of knowledge of the atmospheric and meteorological conditions associated with the precipitation events at Bow Lake, and the numerous factors controlling scavenging, makes it difficult to speculate on whether the efficiency of scavenging may have been higher in 1996/97 than in 1997/1998.

The back trajectory analyses show that there were some differences in the origin of air masses and/or precipitation at Bow Lake between December–March 1996/1997 and December–March 1997/ 1998. A higher number of air masses originated from the S.W. United States and the S.W. Pacific in 1997/1998 than in 1996/1997, when a higher number of air masses originated from British Columbia and Alberta, and the North West (Figure 5.9). In both years the majority of the snowfall (at Sunshine Village) occurred on days when air masses at Bow Lake originated from the S.W. Pacific and S.W. United States, but there was much more snow in 1996/1997 than in 1997/1998 (Figure 5.9). This indicates that inter-annual differences in the dominant source regions of air masses and precipitation (25-37% more snow fall when air masses originated from S.W. US and S.W. Pacific in 1996/1997) might explain part of the 40-90% difference between the March 1997 and March 1998 snowpack OC concentrations (Table 5.8). This is especially true since trans-pacific transport from Asia is sometimes associated with high atmospheric OC concentrations (Bailey et al., 2000).

The retention of contaminants within the snowpack over the course of the winter months depends on factors such as accumulation rates, total accumulation, and air temperatures. Increases in temperature decrease the storage and sorption capacities of the snow for OCs (Wania, 1997; Wania et al., 1998). The time of surface exposure and depth of burial of OCs in the snowpack will influence the degree of volatilization because OCs in the snowpack move by vapour diffusion, and snow and contaminants at the surface are susceptible to sublimation, (Wania, 1997; Wania et al., 1998). Lower accumulation (shallower depth of burial), lower accumulation rates (longer duration of surface exposure between snowfalls), and higher air temperatures will all increase the potential for losses of contaminants from the snowpack following deposition. Mean February and March air temperatures at Bow Summit were slightly lower in 1997, but not significantly different from 1998 (<1.5°C mean difference, SD of means ± 3-5°C, Table 5.13). The snowpack data from Bow Lake indicate that there was only an 11% difference in the snowpack SWE between years. However, the snow pillow data from Sunshine Village indicate that both total snow accumulation and the average rate of accumulation were substantially higher (34% higher SWE, and 37% higher accumulation (mm/day)) in 1997 than in 1998 (Table 5.14). Although the total snowfalls were always greater in 1997, there was little difference in the seasonality of snowfall between the two winters, except that December 1997 received a slightly higher proportion of the total snow fall, than December 1996 (Table 5.15). These results suggest that the combination of higher total snow accumulation and accumulation rates, and lower air temperatures in 1997 may explain a large part of the inter-annual differences in the snowpack OC burdens

5.5.2 Behaviour of OCs during snowmelt

The higher enrichment in the 1st meltwater samples relative to the 2nd samples in 1997, and higher enrichment of the more soluble compounds (HCHs and Endosulphans) relative to the more hydrophobic/less soluble PCBs and DDTs (Figure 5.6), are consistent with the results of other studies of the behaviour of OC contaminants in snowmelt (Schöndorf and Herrmann, 1987; Simmleit et al., 1986; Wania, 1997; Wania et al., 1999). These studies show that as liquid water is formed in the snowpack, the soluble HCHs partition strongly into that phase. This results in the concentration of these compounds in the first fraction of the melt (70-80% of snowpack load in the first 25-40% of the melt (Schöndorf and Herrmann, 1987; Simmleit et al., 1986). DDT and PCBs do not tend to show a first flush behaviour, but are concentrated in the final phases of the melt because of their association with particulate organic matter (Wania, 1997; Wania et al., 1999).

The higher enrichment of α-HCH relative to γ-HCH (Figure 5.6) is counter intuitive since α-HCH is less soluble and has a higher H constant than γ-HCH (Table 5.1). Other researchers have also reported slightly higher enrichment factors for α-HCH vs. γ-HCH (Simmleit et al., 1986), but the differences are much lower than those observed in this study. Given the similarity of the physical properties of Endosulphans and HCHs (Table 5.1), the relatively high enrichments of Endosulphan during snowmelt are not surprising. The lower enrichments of the Endosulphans relative to HCHs probably result from their lower aqueous solubility relative to HCHs (Table 5.1). The higher enrichment of β-Endosulphan over α-Endosulphan indicates that volatilization was not very important during the melt (since β–Endosulphan is much more volatile than α-Endosulphan, Table 5.1), but rather that solubility was the dominant factor influencing the enrichment of the Endosulphan in the meltwater. The solubility of Dieldrin also appears to have been sufficient to result in slight but consistent enrichment of Dieldrin in the 1st melt samples (Figure 5.6). However, Dieldrin was not enriched as much, nor as frequently in the snowmelt as α-Endosulphan (Figure 5.6), even though Dieldrin is more soluble than α-Endosulphan (Table 5.1). This suggests that the relatively high vapour pressure or the high log K_{ow} of Dieldrin must also have had an important effect on the release of this contaminant from the snowpack.

The general lack of enrichment of HCB is likely primarily the result of its relatively low solubility and relatively high log K_{ow}. The depletion of DDT was also likely driven by its high hydrophobicity and affinity for particulate organic carbon (POC) within the snowpack during the melt (Wania, 1997; Wania et al., 1999). Using a model of the partitioning of organic chemical during the settling and melting of a snowpack, Wania (1997) determined that, after melting, 88% of HCB had volatilized, and only 12% had drained with the meltwater. On the other hand, only 14% of DDT was volatilized, and 2% drained, while most of this compound (84%) was bound to OC after snowmelt. The enrichment of ΣDDT in the snowmelt in 1998 is therefore remarkable. The concentrations for ΣDDT in the melt waters are reasonably similar in 1997 and 1998, but the concentrations of DDT in the 1998 snowpack samples were almost always below detection limits (Table 5.7 and 5.9). The enrichment observed for ΣDDT in 1998 snowmelt, may therefore be the result of analytical uncertainties (underestimation) of the concentration of DDT in the 1998 snowpack. It is otherwise difficult to explain these very large enrichments, unless there was a significant difference in the abundances of POC/DOC in the snowpack between years. Higher POC content could reduce the concentration of DDT that drains with meltwater, while higher DOC could increase the apparent dissolved concentrations of DDT (because contaminants sorbed to DOC are not filtered out in the analysis). However, we have no record of the POC/DOC content of the snow for 1997 and 1998.

The finding that snowpack and meltwater concentrations of PCBs were approximately equal is consistent with the observations of Wania et al. (1999) that most PCBs drain in the early to middle stages of the snowmelt. The occasional enrichment of the heavier PCB homologues suggests that volatilization was the dominant loss process rather than adsorption to POC. Volatilization would lead to the preferential loss of the lower (lighter) homologue groups over the heavier and less volatile higher homologues, while adsorption to POC would likely result in greater losses of the heavier more hydrophobic PCBs. The inconsistent behaviour of PCBs (especially for the heavier PCBs) in the meltwater from different sites (Figure 5.6), suggests there were probably large differences in the abundance of POC and/or DOC between the lysimeter sites.

A correlation matrix for the enrichment of the OC pesticides (PCBs were not included) in the first snowmelt samples and the physical properties of OCs supports the observation that aqueous solubility and K_{ow} are the dominant factors controlling the concentration of contaminants in snowmelt (Table 5.16). The OC enrichments were most strongly correlated with solubility (significant at $p<0.05$ in 1997), and to a lesser extent with log K_{ow} (Table 5.16). The correlations for 1998 enrichments were much weaker than in 1997, but the values for solubility and log K_{ow} increased substantially when the DDT enrichments, which were very high in 1998, were excluded from the analysis (Table 5.16).

5.5.3 OC concentrations in runoff

In 1997 the only stream sample to display any significant enrichment of OCs relative to the snowpack at the end of March, was a sample from the Glacial stream collected during the rising limb of what was identified as a snowmelt event on June 7th (Figure 5.7a, Table 5.11). The samples taken towards the end of snowmelt in 1998 were also enriched relative the March snowpack (Figure 5.8, Table 5.12). The enrichments in the stream samples during these snowmelt periods were however usually lower than observed for snowmelt from the lysimeters, suggesting that there were additional losses due to either retention or volatilization during the routing of early season snowmelt to the stream, or dilution by melt water from areas where snowmelt is nearing the end. The low DOC concentrations in the Glacial stream (usually below 1ppm, even during snowmelt) and the nature of the DOC in the stream indicate that only a small fraction of snowmelt passes through soil covered or vegetated areas in this catchment (Chapter 3). This suggests that retention of OCs due to sorption was probably not very important in this catchment. The relatively strong enrichment in the heavier PCBs in this sample (Figure 5.7) also suggests that sorption was not very important in removing OCs from runoff. If sorption were important these heavier PCBs would likely be depleted in runoff, especially relative to the lighter (less hydrophobic, but more volatile) PCBs, due to their higher affinity for organic matter. DOC in the runoff could increase the relative solubility of the heavier PCB compounds in the meltwater. DOC concentrations in this stream are, however, likely too low to have a significant effect on the solubility of the PCBs (Chiou et al., 1986).

The high enrichment of OCs in the Glacial stream relative to the Bow River (compare June 7th with June 9th 1997 (Figure 5.7), and May 8th with May 9th 1998 (Figure 5.8)) suggests that there were greater OC losses during the routing of early season snowmelt to the stream in the Bow River catchment than in the Glacial catchment. The concentration of DOC in the Bow River is usually relatively high (around 1.5-2.0 ppm) during the early snowmelt, and the pulse of DOC in the Bow River at the onset of snowmelt appears to be flushed to the stream from soils by shallow subsurface flow (Chapter 3). The large differences in DOC concentrations between the two streams suggest that the greater losses are likely due to higher sorption of OCs to soils or to DOC during the routing of melt water in the Bow River catchment. The results from the snow samples also suggest that some of the differences may be due to lower average snowpack OC concentrations in this catchment, as a result of the larger proportion of forest covered area in the Bow River catchment. If the enrichments for the Bow River samples are calculated using the mean OC concentrations in snow from only the forested sites instead of the average values (Table 5.6), the depletions for most OCs are reduced slightly, but none of the contaminants are significantly enriched in any of the samples. This indicates that retention of OCs due to flow routing has a larger impact on stream OC concentrations than the lower initial OC concentrations in forested/soil covered catchments.

The strong and persistent 12 and 24 hour scale power in the Glacial stream discharge wavelet spectrum ($W_n^{QQ}(24hr)$ and $W_n^{QQ}(12hr)$) during July and August 1998 indicates that there was significant exposure of glacial ice, and probably the development of major channels within the glacial drainage system late in the summer (Lafrenière and Sharp, 2003). The enrichment of α-HCH, and ΣDDT in the Glacial stream samples collected between June and August, was often higher than the enrichments observed in the snowmelt beneath the snowpack (Figure 5.6 and Figure 5.8). This indicates that there was little loss of contaminants from meltwater derived from glaciated areas prior to reaching the stream, and/or that glacial water sources (i.e. ice and firn) had higher concentrations of these OCs than the winter snow. Studies in the Canadian Rockies have shown that the concentration of many OC contaminants in ice formed between 1970-1990 are equal to or higher than the concentrations found in contemporary snow (Blais et al., 1998; Donald et al., 1999). However, the very high enrichments in these samples could also be the result of OCs that were retained in the snow/firn aquifer in low melt years (like 1997), stored (frozen) over winter, and then flushed during high melt years, such as 1998. It is also possible that OCs in meltwaters from the firn aquifer at the end of the previous summer were trapped in englacial or subglacial channels in the fall as channels closed over winter (Fountain and Walder, 1998), and that these contaminants were flushed the following summer.

The enrichment of α-HCH, and γ-HCH in the July 25th and August 9th 1998 samples from the Bow River is consistent with interpretations of the discharge hydrographs. These show a persistent diurnal cycle in the Bow River discharge in July and August (Lafrenière and Sharp, 2003), indicating that there was a continuing input of melt induced runoff from the small area of ice cover in the catchment (Figure 5.2). However, the lower enrichments in the Bow River relative to the Glacial stream (Figure 5.8a) indicates that there was either greater loss/retention of OCs en route to the stream relative to the Glacial catchment or that glacier melt comprised a smaller proportion of the total runoff. The DOC concentrations in the Bow River at the end of summer 1998 are much lower than in the spring runoff from this catchment, and they are only marginally higher than in the Glacial stream at this time of year (Chapter 3). Thus, neither flow routing through organic rich environments, nor the differences in DOC concentrations between the two streams are likely to explain the large discrepancies in dissolved OC concentrations in runoff from the two catchments at the end of 1998. OC enrichments are probably lower in the Bow River than in the Glacial stream in late summer 1998 because glacier melt only accounts for a small fraction of the total water flux from this stream, which is groundwater dominated (and DOC/OC poor) at this time of year.

5.5.3.1 Inter-annual differences in OC concentrations in the snowpack and streams

One of the most interesting results of this study is that the concentrations of OCs in runoff were not simply a function of the OC concentration in the previous winter's snowpack. Given the much higher OC concentrations in the snow (Table 5.8), and the higher total accumulation in 1997, and the much higher enrichments in the 1997 snowmelt samples (Table 5.9), it is surprising that the OC concentrations in the streams were only slightly higher in 1997 than in 1998. Despite the substantially lower OC concentrations in the snowpack, the fluxes of several dissolved OCs from the Glacial catchment in 1998 were greater on average than in 1997 (Blais et al., 2001b). The enrichments in 1998 runoff were also higher than in 1997 in both the spring and late summer. This indicates that the extent of glacial ablation was an important control on the release of OCs from the catchments. These observations suggest that (a) older contaminated ice (formed after ~1950) melt contributed significant OCs to runoff in 1998, and/or that (b) the OCs from snow in 1997 may not have been completely flushed during the melt that year, and that some 1997 OC residues (i.e. in firn or ice) were flushed by the extensive melt in

1998. The flushing of OCs through the thin snowpack in 1998 might have resulted in more efficient release of OCs, but the lower OC enrichments in the snowmelt in 1998 relative to 1997 suggest that this is unlikely. The minimal difference observed in the OC concentrations in the Bow River between 1997 and 1998, suggest that in this catchment retention may be the dominant control on the flux of OCs to this stream. In other words, catchment retention captures such a large proportion of available OCs, that the original snowpack burden has little effect on the flux of OCs to the streams

5.6 CONCLUSIONS

The concentration of OCs in the snowpack in a given year can vary substantially over relatively small distances and at the catchment scale. This indicates that a careful description of the physical structure and the DOC/POC content of the snow being sampled and, ideally, multiple samples from a given site are necessary to assure confidence in OC results from snow. This is especially true for studies in forested areas. The presence of forests appears to reduce the total accumulation and increase volatilization losses of snow and contaminants. It might therefore contribute to the observed increase in contaminant deposition with elevation (Blais et al., 1998), since forest cover decreases with increasing elevation. These changes are probably the result of the interception and sublimation of snow and contaminants in the canopy, and enhanced volatilization from the relatively thin snow pack on the forest floor.

The difference between the OC concentrations in March 1997 and March 1998 snow was not apparently related to changes in usage or emission patterns. The results indicate that the combination of more precipitation from air masses originating from the S.W. Pacific and S.W. U.S., higher total snow accumulation and accumulation rates, and lower air temperatures in 1997 most likely explain the inter-annual differences in the snowpack OC burdens. The degree of enrichment of a compound in snowmelt relative to snow was strongly related to the aqueous solubility and octanol-water partitioning coefficient of the chemical, rather than vapour pressure or air-water partitioning. One of the major limitations of this study was the lack of knowledge of the abundance of DOC and POC in the snow and snowmelt samples. Without these measurements we cannot fully explain the inter site and inter-annual variability in the enrichments of the more hydrophobic ΣDDT and PCBs in the snowmelt samples.

In the streams, OCs were only enriched during snowmelt and in late summer 1998 when there was significant exposure of glacial ice. The significant enrichments in the Glacial runoff and little or no enrichment in the Bow River during snowmelt, are probably largely due to the higher sorption of OCs to soils or vegetation during the routing of melt water in the Bow River catchment. The impact on the Bow River OC concentrations of lower accumulation of OCs in the snow as a result of forest cover appeared to be small relative to the effect of catchment retention. However, the results suggest that further research on the impact of vegetation on the overall fate of OCs in alpine environments is needed. Since, the extent of forests is usually well known and easy to map digitally, it should be relatively easy to incorporate this variable into predictive models to determine areas at risk of OC contamination.

The very high OC enrichments and relatively high OC concentrations in the Glacial stream in 1998 indicate that the amount OCs in glacial runoff was not simply a function of the OC concentration in the previous winter's snowpack. The results suggest that the concentration (and flux) of contaminants in glacial runoff will depend on the OC burden of the current winter's snowpack, the extent of melt and glacial ablation, as well as the snowpack OC burden and melt conditions the previous year. Thus, lower snowfalls (and snowpack OC burdens) and higher glacial ablation (i.e El Nino conditions) may yield higher annual OC fluxes than years when annual snow accumulation and OC burden are higher.

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Table 5.1 Physical and Chemical Properties of selected OC pesticides (Mackay et al., 1992b) and PCBs (Mackay et al., 1992a). Uses and current status from (UNEP, 2002a; UNEP, 2002b; UNEP, 2002c; UNEP, 2002d), ** (de March et al., 1998), and *** (Li, 1999). P_L is the super cooled liquid vapour pressure, C_L is the aqueous solubility, log K_{ow} is the log of the octanol-water partitioning coefficient (a measure of hydrophobicity), H is the Henry's law constant (a measure of air-water partitioning).

Compound	Formula	P_L (Pa 25°C)	C_L (mol/m^3)	log K_{ow}	H (Pa m^3/mol)	Uses	Status North America	Status W. Europe	Status Asia, E. Europe, and other
α-HCH	$C_6H_6Cl_6$	0.1000	0.1150	3.81	0.87	Insecticide	Canada and US, Mexico: banned (1971, 1976, and 1993)**	Banned in all countries (1970-1990)**	China: banned (1983), Former Soviet Union (FSU): banned 1990; Banned in S.E. Asia; India, Brazil, Columbia: still in use as of 1996**
γ-HCH	$C_6H_6Cl_6$	0.0274	0.1840	3.70	0.15	Insecticide (seed dressing)	Canada: sales ceased 2001, prohibited 2004, US: most uses cancelled (1983), Mexico: in use.	Restricted or banned in most of W. Europe	Banned in most of S.E. Asia; banned in N.E. and Central Asia, restricted use in China; Middle East and India: No Information
HCB	C_6Cl_6	0.2447	0.0019	5.50	131.00	Fungicide, insecticide, manufacturing by-product	Canada and Mexico: prohibited, US: registration ended (1984)	Prohibited or withdrawn in most countries***	Banned in Middle East and India; Banned in S. E. Asia. ; restricted in N.E. and Central Asia, Singapore, Phlippines
Dieldrin	$C_{12}H_8Cl_6O$	0.0160	0.0142	5.20	1.12	Insectide (soil insects), termiticide	Canada: restricted (1987), US: banned (1971), Mexico: prohibited	Prohibited in most countries***	Banned or restricted in Middle East and India; banned in N.E. and Central Asia; banned in S.E. Asia
α-Endosulphan	$C_9H_6Cl_6O_3S$	0.0080	0.0080	3.62	1.00	Insectide (fruit, vegetables, tobacco)	Canada and US, Mexico: Still in use	Still in use***	India, Nepal, Pakistan: still in use; Banned in Middle East
β-Endosulphan	$C_9H_6Cl_6O_3S$	0.3940	0.0710	3.83	5.55				
o,p-DDT	$C_{14}H_9Cl_5$		0.0005		0.35	Insecticide	Canada: prohibited (1990), US: Banned (1972), Mexico: restricted	Prohibited in most countries***	Banned in Middle East, restricted use in India; banned in most of N.E. and Central Asia, restriced in Russia and Kazakhstan
p,p-DDT	$C_{14}H_9Cl_5$	0.0001	0.0001	6.19	2.36				
p,p-DDE	$C_{14}H_8Cl_4$	0.0037	0.0005	5.70	7.95	Breakdown product of DDT			
o,p-DDE	$C_{14}H_8Cl_4$	0.0034	0.0014	5.80	2.54				
o,p-DDD	$C_{14}H_{10}Cl_4$	0.0014		6.00					
p,p-DDD	$C_{14}H_{10}Cl_4$	0.0007	0.0011	5.5	0.64				
PCBs									
Mono-Cl	$C_{12}H_9Cl$	0.9-2.5	13.24-35.66	4.3-4.6	42.56-75.55	Used as insulating or heat exchange fluids (mainly in transformer and capacitor oils), and as lubricanting or cutting oils	Canada, US and Mexico: new uses Pohibited; closed uses allowed	All uses banned in most countries	Banned in Middle East, India; still in use in Russia and Kazakhstan, restricted in N.E. and Central Asia; banned in most of S.E. Asia, restricted in Malaysia and Signapore
Di-Cl	$C_{12}H_8Cl_2$	0.008-0.60	4.56-10.14	4.9-5.3	17.0-92.21				
Tri-Cl	$C_{12}H_7Cl_3$	0.003-0.22	0.24-2.39	5.5-5.9	24.29-92.21				
Tetra-Cl	$C_{12}H_6Cl_4$	0.002	0.133-1.30	5.6-6.5	1.72-47.59				
Penta-Cl	$C_{12}H_5Cl_5$	0.0023-0.051	0.093-0.337	6.2-6.5	24.8-151.4				
Hexa-Cl	$C_{12}H_4Cl_6$	0.0007-0.012	0.0061-0.0286	6.7-7.3	11.9-818				
Hepta-Cl	$C_{12}H_3Cl_7$	0.00025	0.0191-0.046	6.7-7.0	5.4				
Octa-Cl	$C_{12}H_2Cl_8$	0.0006	0.0098-0.0158	7.1	38.08				
Nona-Cl	$C_{12}HCl_9$		0.00141-0.0146	7.2-8.16					
Deca-Cl	$C_{12}Cl_{10}$		0.00144	8.26	20.84				

Table 5.2 Analytical method detection limits (MDLs) for OC pesticides and PCB homologue groups

OC pesticides	MDL (pg/L)	PCB Homologues	MDL (pg/L)
α-HCH	2.2	Mono	10.2
γ-HCH	1.4	Di	12.0
HCB	0.4	Tri	16.3
Dieldrin	1.1	Tetra	26.3
α-Endosulfan	1.0	Penta	20.2
β-Endosulfan	2.1	Hexa	23.1
p,p-DDE	0.9	Hepta	20.2
p,p-DDD	1.5	Octa	11.7
o,p-DDT	1.3	Nona	4.5
p,p-DDT	1.6	Deca	1.1

Table 5.3 The means and standard deviations (SD) of extraction efficiencies for the lab surrogates

	1,3-DBB	Endrin Ketone	PCB 30	PCB 204
Mean *(n=50)*	70	63	54	71
SD	24	35	32	30

Table 5.4 OC concentrations (pg/L) for 1997 March snow samples. See Figure 2 for site locations. Samples labeled 'Forest' and 'Open' were taken adjacent to the corresponding snowmelt lysimeter (Figure 2). Σ PCBs congeners include (dashes represent co-eluting PCBs): 1, 3, 4-10, 7-9, 6, 8-5, 19, 12-13, 18, 15-17, 24-27, 16-32, 54-29, 26, 25, 50, 31-28, 33-20-53, 51, 22, 45, 46, 52, 49, 43, 48-47, 44, 59-42, 64-41-71, 40, 100, 63, 74, 70-76-98, 66-95, 91-55, 56-60, 92, 84, 101, 99, 119, 83, 97, 87-81, 85, 136, 110, 82, 151, 135-144, 147-107, 149, 118, 133, 114, 134-131, 146, 153-132-105, 141-179, 137, 176-130, 163-138, 158, 129, 178, 175, 187-182, 183, 128, 167, 185, 174, 177,202-171, 156, 173, 157-200, 172, 197, 180, 193, 191, 199, 170-190, 198, 201, 203-196, 189, 206-195, 207, 194, 205, 208, 209.

Sample	Date	SWE (mm)	α-HCH	γ-HCH	HCB	Dieldrin	α-Endosulphan	β-Endosulphan	ΣDDT	Σ PCB	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta
Site 3	24-Mar-97	366	370	210	15	43	230	66	23	1500	75	42	170	830	200	130	75
Site 4	25-Mar-97	384	430	230	28	39	250	70	33	1600	36	35	210	840	220	160	82
Site 5	30-Mar-97	373	380	210	12	45	300	130	36	1500	110	88	170	780	140	120	77
Site 6	30-Mar-97	325	360	240	21	35	300	180	51	2000	110	94	200	1000	200	150	220
Site 7	29-Mar-97	251	100	77	4.9	27	180	78	3.9	1300	370	80	250	260	200	120	36
Site 8	29-Mar-97	165	48	66	8.6	35	110	32	9.2	1500	0	160	440	430	280	170	39
Site 10	30-Mar-97	90	150	96	3.9	32	220	50	26	826	43	42	220	220	160	100	30
Site 11	30-Mar-97	218	210	150	11	33	240	64	2.2	1300	74	130	360	340	220	140	32
Site 12	30-Mar-97	193	240	130	6.1	34	240	68	14	902	65	56	220	250	180	92	27
Site 13	30-Mar-97	201	110	100	9.1	30	190	34	4.6	1300	200	73	290	330	230	120	40
Site 14	1-Apr-97	297	300	160	5.0	25	290	76	8.1	870	10	47	230	280	200	74	26
Forest	23-Mar-97	318	80	62	7.9	28	80	26	61	1300	620	89	250	170	110	71	19
Open	24-Mar-97	373	290	280	19	74	740	1300	0	1700	0	210	450	490	280	170	59
	Mean	273	240	150	12	37	260	170	21	1400	130	88	270	480	202	130	59
	SD	94	130	72	7.2	12	160	350	20	300	180	52	94	290	48	33	53
	CV%	34	54	47	62	34	62	206	94	21	138	58	35	60	24	26	90

Table 5.5 Correlation coefficients for OC concentrations with respect to snowpack SWE (mm) for 1997 samples.

	SWE (mm)	α-HCH	γ-HCH	HCB	Dieldrin	α-Endosulphan	β–Endosulphan	ΣDDT	Σ PCB
	1	*0.71*	*0.70*	*0.65*	0.43	0.32	0.45	0.49	*0.56*
SWE (mm)	p= —	*p=.009*	*p=.011*	*p=.021*	p=.160	p=.316	p=.140	p=.110	*p=.056*

Table 5.6 Means, standard deviations and CVs for OC concentrations in 1997 snowpack samples, according to whether they were from predominantly forested or non-forested sites. Δ is the difference in the mean concentrations, Δ% is the percent difference, Significance (p) is the p value of the z–test for the sample means, with a hypothesized mean difference of zero.

Sample	Date	SWE (mm)	Density (g/cm^3)	α-HCH	γ-HCH	HCB	Dieldrin	α-Endosulphan	β–Endosulphan	ΣDDT	ΣPCB	α-HCH/ γ-HCH	HCB/ Dieldrin	β–Endosulphan/ α-Endosulphan	(αHCH+γHCH) /ΣPCB
Site 3	24-Mar-97	366	0.23	370	210	15	43	230	66	23	1500	1.76	0.35	0.29	0.39
Site 4	25-Mar-97	384	0.24	430	230	28	39	250	70	33	1600	1.87	0.72	0.28	0.41
Site 5	30-Mar-97	373	0.28	380	210	12	45	300	130	36	1500	1.81	0.27	0.43	0.39
Site 6	30-Mar-97	325	0.23	360	240	21	35	300	180	51	2000	1.50	0.60	0.60	0.30
Open	24-Mar-97	373	0.25	290	280	19	74	740	1300	0.0	1700	1.04	0.26	1.76	0.34
Site 14	1-Apr-97	297	0.20	300	160	5.0	25	290	76	8.1	870	1.88	0.20	0.26	0.53
	Mean	353	0.24	350	220	17	43	350	360	25	1500	1.64	0.40	0.60	0.39
	SD	34	0.03	52	40	8	16	190	550	19	370	0.33	0.21	0.58	0.08
	CV%	*10*	*11*	*15*	*18*	*47*	*38*	*54*	*153*	*75*	*25*	*20*	53	*96*	*20*
Site 7	29-Mar-97	251	0.20	100	77	4.9	27	180	78	3.9	1300	1.29	0.18	0.43	0.14
Site 8	29-Mar-97	165	0.21	48	66	8.6	35	110	32	9.2	1500	0.73	0.24	0.30	0.08
Site 10	30-Mar-97	90	0.06	150	96	3.9	32	220	50	26	826	1.56	0.12	0.23	0.30
Site 11	30-Mar-97	218	0.17	210	150	11	33	240	64	2.2	1300	1.40	0.32	0.27	0.28
Site 12	30-Mar-97	193	0.16	240	130	6.1	34	240	68	14	900	1.85	0.18	0.28	0.41
Site 13	30-Mar-97	201	0.15	110	100	9.1	30	190	34	4.6	1300	1.10	0.30	0.18	0.16
Forest	23-Mar-97	318	0.20	82	62	7.9	28	80	26	61	1300	1.32	0.29	0.33	0.11
	Mean	205	0.16	140	97	7	31	180	50	17	1200	1.32	0.23	0.29	0.21
	SD	71	0.05	70	33	2.4	3.1	63	20.1	21	250	0.35	0.08	0.08	0.12
	CV%	*34*	*30*	*50*	*34*	*33*	*10*	35	*40*	*121*	*21*	*27*	*32*	*28*	*58*
Δ (pg/L)		148	0.07	210	120	9.3	12.0	170	310	7.8	310	0.3	0.2	0.3	0.2
%Δ		53	36	86	76	78	32	64	151	37	23	22	52	71	61
Significance (p)		0.000	0.000	0.000	0.000	0.003	0.035	0.002	0.124	0.242	0.043	0.051	0.035	0.091	0.001

Table 5.7 OC concentrations (pg/L) for 1998 snow samples from sites adjacent to the snowmelt lysimeters.

Sample	Date	SWE (mm)	α-HCH	γ-HCH	HCB	Dieldrin	α-Endosulphan	β–Endosulphan	ΣDDT	Σ PCB	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta
Open a	25/3/98	259	16	21	2.3	8.4	66	28	5.2	970	0.0	59	220	300	250	110	25
Open b	25/3/98	259	9.9	27	4.0	22	73	20	3.5	1100	0.0	80	310	330	220	110	23
Open c	25/3/98	259	6.1	28	6.8	11	22	10	0.0	960	0.0	64	290	280	200	99	21
Forest a	25/3/98	229	42	43	3.3	49	160	58	7.3	1700	24	86	400	510	420	210	41
Forest b	25/3/98	229	57	37	2.5	6.9	56	20	6.6	490	29	39	140	130	78	51	16
Forest c	25/3/98	229	33	42	3.5	9.8	80	41	0.0	680	0.0	54	240	180	110	78	21
All (n=6)	Mean	244	27	33	3.7	18	76	29	3.8	980	8.8	64	270	290	210	110	24
	SD	16	20	9.1	1.6	16	46	17	3.2	420	14	17	88	130	120	54	8.6
	CV%	7	74	28	44	91	60	59	85	43	156	27	33	45	57	49	35
Open (n=3)	Mean	259	11	25	4.4	14	54	19	2.9	1000	0.0	68	270	300	220	110	23
	SD	28	4.8	3.9	2.3	7.1	28	8.8	2.6	78	0.0	11	47	25	25	6.6	1.7
	CV%	11	*45*	*16*	*53*	*52*	*52*	*45*	*91*	*8*		16	18	8	11	6	7
Forest (n=3)	Mean	229	44	41	3.1	22	99	39	4.6	960	18	60	260	270	200	110	26
	SD	14	12	3.3	0.5	23	54	19	4.0	650	15	24	130	210	190	85	13
	CV%	6	*28*	*8*	*17*	*107*	*55*	*49*	*87*	*68*	88	41	50	78	95	77	52

Table 5.8 A comparison of the mean snowpack SWE and OC concentrations (pg/L) for 1997and 1998, where % Change is the difference between the ratio of the 1998 values to the 1997 values as percent (% Change = 1998/1997*100 – 100). Thus a negative change represents a decrease in 1998 relative to 1997.

Sample		SWE (mm)	α-HCH	γ-HCH	HCB	Dieldrin	α-Endosulphan	β–Endosulphan	ΣDDT	Σ PCB	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta
March 1997 Snow (n=13)	*Mean*	273	240	154	12	37	260	170	21	1400	130	88	270	480	200	130	58
	SD	94	130	72	7.2	12	160	350	20	340	180	51	94	290	48	33	52
	CV%	34	54	47	62	34	61	208	94	25	136	58	35	60	24	27	89
March 1998 Snow (n=6)	Mean	244	27	33	3.7	12	76	29	3.8	830	9	64	270	240	170	90	24
	SD	7	20	9.1	1.6	5.9	44	17	3.2	240	14	17	88	84	73	26	8.6
	CV%	3	74	28	44	51	59	59	85	29	156	27	33	35	42	29	35
%Change	1998/1997	-11	-89	-79	-68	-69	-71	-83	-82	-41	-93	-27	0	-50	-15	-31	-58

Table 5.9 OC concentrations (pg/L) for (a) 1997, and (b) 1998 snowmelt samples. F1 and F2 refer to the two lysimeters at the Forest site, and Op1 and Op2 refer to the lysimeters at the Open site (Figure 2) .

a)

Sample	Date	Vol (L)	α-HCH	γ-HCH	HCB	Dieldrin	α- Endosulphan	β– Endosulphan	ΣDDT	Σ PCB	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta
F1_06/05/97	6-May-97	9.9	4000	1300	10	58	130	60	1.5	2500	83	200	290	720	440	290	450
F2_06/05/97	6-May-97	12.3	2800	1100	9.4	71	960	440	12	1200	17	57	150	210	480	150	100
F2_17/05/97	17-May-97	19.7	240	100	7.3	9.1	87	84	5.0	820	98	14	110	170	210	130	90
Op1_03/05/97	3-May-97	17.9	3200	1200	8.9	59	770	290	8.7	1200	0	360	230	200	190	160	70
Op1_16/05/97	16-May-97	5.7	67	39	2.8	5.1	24	16	0.6	1300	6	56	350	300	270	230	90
Op2_03/05/97	3-May-97	3.3	1600	550	19	110	490	321	18	4000	38	410	1182	910	740	470	250
Op2_16/05/97	16-May-97	19.7	ND	ND	8.2	ND	ND	ND	0.0	840	244	120	140	110	120	90	20

b)

Sample	Date	Vol (L)	α-HCH	γ-HCH	HCB	Dieldrin	α- Endosulphan	β– Endosulphan	ΣDDT	Σ PCB	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta
F1_09/05/98	09-May-98	17.8	180	110	3.8	16	150	48	11	1300	15	61	210	250	250	300	150
F2_09/05/98	09-May-98	18.7	170	120	5.7	3.2	nd	9.6	22	5000	0.0	110	440	580	870	1500	1200

Table 5.10 OC concentrations in the Glacial stream (GL) and the Bow River (BR) 1997 and 1998. Q is the mean daily discharge.

Site	Date	Day	Q (m^3/s)	α-HCH	γ-HCH	HCB	Dieldrin	α-Endosulphan	β-Endosulphan	ΣDDT	ΣPCB	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta
GL	06/07/97	158.0	3.2	430	280	10	42	52	39	4.3	1400	0	120	220	320	360	270	88
GL	06/19/97	170.0	5.3	250	150	4.8	23	18	17	0.0	210	0	33	46	48	39	34	10
GL	06/29/97	180.0	1.2	140	77	5.2	21	8.5	15	6.0	210	18	20	36	52	47	25	6.7
GL	07/13/97	194.0	3.1	190	93	6.3	21	16	26	7.1	500	180	77	75	77	39	33	12
GL	07/27/97	208.0	2.4	210	89	6.9	24	14	23	8.1	550	210	52	89	81	65	39	12
GL	08/11/97	223.0	2.8	120	39	2.6	9.4	8.0	22	3.6	170	32	16	24	31	25	36	7.2
GL	08/25/97	237.0	3.7	220	70	4.2	15	16	34	6.2	320	79	30	52	53	42	51	9.1
		Mean	*3.1*	*220*	*110*	*5.7*	*22*	*19*	*25*	*5.3*	*480*	*74*	*50*	*77*	*94*	*88*	*70*	*21*
		SD	*1.3*	*100*	*80*	*2.4*	*10*	*15*	*8.7*	*2.9*	*430*	*87*	*37*	*67*	*100*	*120*	*89*	*30*
		CV%	*41*	*45*	*73*	*41*	*46*	*80*	*35*	*55*	*90*	*118*	*75*	*86*	*106*	*136*	*127*	*143*
GL	05/09/98	129		120	99	8.3	24	20	11	10	810	0	79	190	170	160	180	34
GL	05/18/98	138	0.3	0	0	6.2	13	5.4	7.2	6.0	340	0	38	95	79	63	55	13
GL	06/07/98	158	1.0	140	160	7.7	18	0.0	7.3	36	800	18	15	33	58	140	240	220
GL	06/23/98	174	3.0	160	160	4.2	18	0.0	6.7	13	160	13	11	31	46	35	20	3.6
GL	07/26/98	207	6.4	210	99	5.9	13	6.6	5.1	38	120	12	2.5	14	31	33	23	7.9
GL	08/09/98	221	5.6	210	100	0.5	14	3.5	4.1	32	13	1.0	0.3	1.8	3.2	3.7	2.4	0.7
GL	08/26/98	238	4.1	195	67	6.6	10	23	10	31	300	8.2	5.6	23	50	80	89	37
		Mean	*3.4*	*150*	*98*	*5.6*	*16*	*8.4*	*7.3*	*24*	*363*	*7.5*	*22*	*55*	*62*	*73*	*87*	*45*
		SD	*2.4*	*74*	*55*	*2.6*	*4.5*	*9.4*	*2.3*	*13*	*321*	*7.4*	*28*	*66*	*53*	*58*	*90*	*78*
		CV%	*72*	*49*	*56*	*47*	*29*	*112*	*32*	*57*	*88*	*98*	*131*	*120*	*85*	*79*	*104*	*174*
BR	06/09/97	160.0	2.0	42	64	7.6	8.8	12	25	2.6	640	0	79	120	160	140	100	37
BR	06/19/97	170.0	1.8	27	15	3.9	7.9	4.2	9.9	0.0	290	0	44	74	72	48	35	11
BR	06/30/97	181.0	1.0	17	18	4.3	6.9	3.7	7.8	0.0	310	120	35	45	41	29	28	9
BR	07/14/97	195.0	1.2	22	9.0	6.3	7.5	7.8	15	4.1	490	150	53	62	66	110	36	13
BR	07/27/97	208.0	0.6	21	16	5.7	8.6	4.3	22	5.7	470	110	58	110	90	51	43	12
BR	08/11/97	223.0	0.3	14	5.7	2.7	3.8	2.4	18	1.0	200	44	22	37	36	25	30	6
BR	08/24/97	236.0	0.5	20	10	4.2	5.4	1.2	27	4.5	470	130	44	83	79	56	64	12
		Mean	*1.0*	*23*	*20*	*5.0*	*7.0*	*5.2*	*18*	*2.5*	*410*	*79*	*48*	*76*	*78*	*65*	*48*	*14*
		SD	*0.6*	*9.3*	*20*	*1.7*	*1.8*	*3.8*	*7.4*	*2.3*	*150*	*63*	*18*	*31*	*41*	*43*	*26*	*10*
		CV%	*61*	*40*	*102*	*33*	*26*	*74*	*41*	*89*	*37*	*80*	*38*	*41*	*53*	*66*	*54*	*71*
BR	05/08/98	128		17	51	3.7	4.7	9.4	5.0	3.6	890	5	44	110	140	180	220	160
BR	05/17/98	137	0.9	4.9	15	4.9	2.8	3.0	2.4	2.3	310	0	23	88	68	53	61	18
BR	06/06/98	157	0.8	8.4	19	3.8	2.4	0.0	3.0	11	230	3	9	14	26	44	66	53
BR	06/22/98	173	0.9	18	24	4.2	4.8	4.8	1.3	19	110	9	7	12	29	21	20	6
BR	07/26/98	207	0.6	64	25	6.7	7.2	0.7	6.2	17	120	9	3	14	27	32	22	8
BR	08/09/98	221	0.4	71	43	5.4	6.0	4.7	0.0	12	150	15	4	19	39	35	27	7
BR	08/27/98	239	0.2	21	12	5.6	3.9	16	6.2	5.8	140	15	4	18	34	37	27	8
		Mean	*0.6*	*29*	*27*	*4.9*	*4.5*	*5.6*	*3.4*	*10*	*280*	*8*	*13*	*39*	*52*	*58*	*63*	*37*
		SD	*0.3*	*27*	*14*	*1.1*	*1.7*	*5.7*	*2.4*	*6.5*	*280*	*6*	*15*	*41*	*41*	*55*	*72*	*57*
		CV%	*46*	*92*	*54*	*22*	*37*	*102*	*70*	*64*	*100*	*73*	*114*	*105*	*80*	*95*	*113*	*153*

Table 5.11 Summary of discharge, wavelet, snowpack and precipitation data used to assess the principal water sources and flow routing of runoff on sampling days in 1997, where: Q_s is the seasonal mean discharge, $W_n^{QQ}(s)$ is the power for the wavelet spectrum of discharge at scale (s), $W_n^{TT}(s)$ is the power in the wavelet spectrum of temperature, $\theta^{TQ}(24hr)$ is the phase difference between the temperature and discharge at the 24 hour scale.

Site	Date	Day	Q_d (m^3/s)	$(Q_d-Q_s)/Q_s$	W_n^{QQ} (24hr)	Strong W_n^{QQ} (<24hr)	W_n^{QQ} (<96hr)	Rain (mm) in last 72hrs	Strong $Wn^{QQ}(s)$, No Strong $Wn^{TQ}(s)$	Rapid change in $\theta^{TQ}(24hr)$	Water Source(s)	Flow path(s)	Height of Snow (cm) Bow Lake (1940 masl)	SWE (mm) Bow Summit (2080 masl)	SWE (mm) Katherine Lake (2380 masl)	SWE (mm) Sunshine Village (2230 masl)
GL	06/07/97	158	3.2	0.9	1-2.5	day 162 /167	--	3.1	no	no	snow	surface/shallow subsurface	n/a	254	531	473
	06/19/97	170	5.3	1.4	2.5-5	day 167 /170	>20	8.2	no	no	snow	surface/shallow subsurface				
	06/29/97	180	1.8	0.5	0.5-1	none	2.5-5	6.8	no	no	groundwater	baseflow				
	07/13/97	194	2.9	0.8	0.5-1	none	10-20	17.2	no	yes	snow/rain	surface/shallow subsurface				0 (July 7)
	07/27/97	208	2.3	0.6	0.5-1	none	>20	2.4	no	no	snow	glacial				
	08/11/97	223	2.6	0.7	1-2.5	none	>20	0.4	no	no	snow/ice	glacial /supraglacial				
	08/25/97	237	3.5	0.9	1-2.5	none	10-20	12.8	no	no	snow/ice	glacial /supraglacial				
BR	06/09/97	160	2.1	2.0	2.5-5*	day 160	--	1.1	no	no	snow	surface/shallow subsurface				
	06/19/97	170	1.8	1.7	0.5-1	day 160-169	1-2.5	8.2	no	no	snow	surface/shallow subsurface				
	06/30/97	181	0.9	0.9	0.5-1	none	1-2.5	5.7	no	no	groundwater	baseflow				
	07/14/97	195	1.1	1.0	0.5-1	none	0.5-1	12.9	no	yes	snow/ rain /groundwater	surface /baseflow				
	07/27/97	208	0.6	0.6	0.5-1	none	0.5-1	2.4	no	no	snow/groundwater	surface /baseflow				
	08/11/97	223	0.5	0.4	0.5-1	none	1-2.5	0.4	no	no	snow/groundwater	surface /baseflow				
	08/24/97	236	0.6	0.6	0.5-1	none	none	11.3	no	no	groundwater	baseflow				

Table 5.12 Summary of discharge, wavelet, snowpack and precipitation data used to assess the principal water sources and flow routing of runoff for sampling days in 1998, where: Q_s is the seasonal mean discharge, $W_n^{QQ}(s)$ is the power for the wavelet spectrum of discharge at scale (s), $W_n^{TT}(s)$ is the power for the wavelet spectrum of temperature, $\theta^{TQ}(24hr)$ is the phase difference between the temperature and discharge series at the 24 hour scale.

Site	Date	Day	Q_d (m³/s)	$(Q_d-Q_s)/Q_s$	W_n^{QQ} (24hr)	Strong W_n^{QQ} (<24hr)	W_n^{QQ} (<96hr)	Rain (mm) in last 72hrs	Strong $Wn^{QQ}(s)$, No Strong $Wn^{TQ}(s)$	Rapid change in $\theta^{TQ}(24hr)$	Water Source(s)	Flow path(s)	Height of Snow (cm) Bow Lake (1840 masl)	SWE (mm) Bow Summit (2080 masl)	SWE (mm) Katherine Lake (2380 masl)	SWE (mm) Sunshine Village (2230 masl)
	4/30/98												25	254	343	421
GL	05/09/98	129	–	–	–	–	–	1.1	–	–	snow	surface/shallow subsurface	0 (May 3)			
	05/18/98	138	1.0	0.3	no	no	n/a	6.8	no	no	snow	surface/shallow subsurface				
	06/07/98	158	1.3	0.3	1-2.5	no	5-10	11.0	no	no	snow	glacial		0 (May 29)	0 (June 7)	29 (June 1)
	06/23/98	174	2.8	0.7	0.5-1	no	1-2.5	0.0	no	no	snow	glacial				
	07/26/98	207	6.9	1.8	10-20*	no	10-20	0.0	no	no	snow/ice	glacial				
	08/09/98	221	5.7	1.5	10-20*	yes	>20	2.1	no	no	snow/ice	glacial /subglacial?				
	08/26/98	238	3.9	1.0	10-20*	yes	10-20	4.3	no	no	snow/ice	glacial /subglacial?				
BR	05/08/98	128	–	–	–	–	–	1.1	–	–	snow	surface/shallow subsurface				
	05/17/98	137	0.7	1.2	no	day 136	–	5.3	yes	day 136	snow/rain	surface /subsurface				
	06/06/98	157	0.8	1.3	no	no	5-10	7.2	yes	no	snow/rain /groundwater	surface /subsurface				
	06/22/98	173	0.9	1.5	no	no	1-2.5	0.0	no	no	groundwater	surface /subsurface				
	07/26/98	207	0.5	0.9	2.5-5*	no	0.5-1	0.0	no	no	snow/ice/ groundwater	glacial/snow				
	08/09/98	221	0.4	0.6	1-2.5*	no	0.5-1	2.1	no	no	snow/ice/ groundwater	glacial? /baseflow				
	08/27/98	239	0.2	0.4	0.5-1*	no	no	4.3	no	no	snow/ice/ groundwater	glacial? /baseflow				

Table 5.13 Average monthly air temperatures at Bow Summit for January, February and March, in 1997 and 1998.

		Mean T (ºC)	SD
1997	Jan	-12.2	7.4
	Feb	-8.6	4.0
	Mar	-8.5	4.9
1998	Jan	-12.7	8.1
	Feb	-7.7	3.4
	Mar	-7.0	4.3

Table 5.14 Snowfall statistics from Sunshine Village for 1997 and 1998 (data provided by Alberta Environment).

	1997	1998
# Snowfall Days	80	70
# Days with > 3 mm SWE/day	51	30
Average mm/day (Dec-Mar)	4	2.6
Total SWE mm (end of March)	442	668

Table 5.15 Seasonality of snowfall at Sunshine Village for 1997 and 1998 (data provided by Alberta Environment).

	SWE (mm)		% of Total	
	1997	1998	1997	1998
Before December	175	117	26	26
December	125	124	19	28
January	164	73	25	17
February	60	32	9	7
March	141	95	21	21

Table 5.16 Correlations between mean enrichment of OCs in the first melt water samples and the physical properties of contaminants: liquid vapour pressure (P_L), aqueous solubility (C_L), octanol-water partitioning coefficient (log K_{ow}), and Henry's law constants (H). The correlations were determined using the enrichments for HCHs, Endosulphans, HCB, Dieldrin and ΣDDT (N=7) for 1997, 1998. The correlations were also determined for 1998 excluding ΣDDT. Correlations >0.75 are significant at $p < .05$.

	1997	1998	1998 (excluding DDT)	P_L (Pa 25°C)	C_L (mol/m^3)	log K_{ow}	H (Pa m^3/mol)
1997	1.00			-0.02	0.76	-0.65	-0.34
1998		1.00		-0.35	0.44	-0.16	-0.31
1998 (excluding DDT)			1.00	-0.27	0.63	-0.50	-0.28
P_L (Pa 25°C)				1.00	0.01	-0.12	0.41
C_L (mol/m^3)					1.00	-0.65	-0.35
log K_{ow}							0.45
H (Pa m^3/mol)							1.00

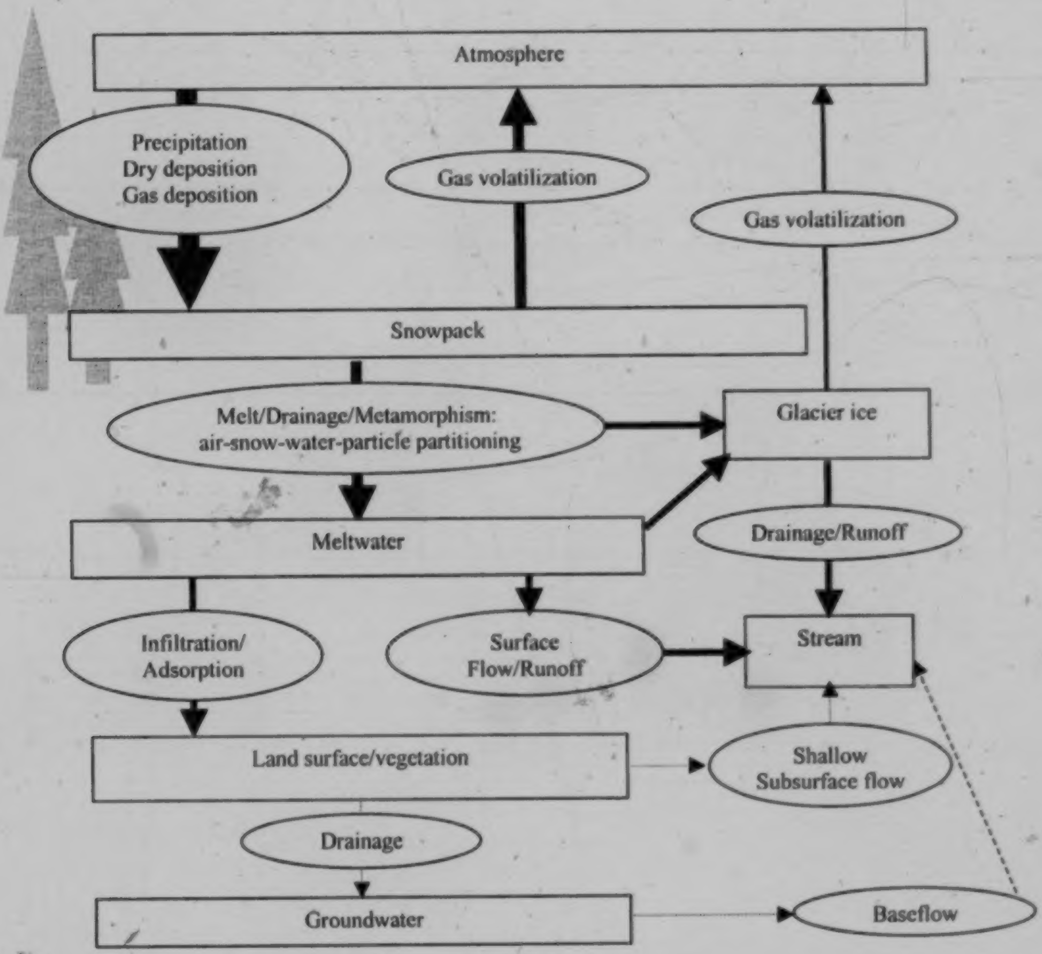
Atmosphere
Precipitation
Dry deposition
Gas deposition
Gas volatilization
Gas volatilization
Snowpack
Melt/Drainage/Metamorphism:
air-snow-water-particle partitioning
Glacier ice
Meltwater
Drainage/Runoff
Infiltration/
Adsorption
Surface
Flow/Runoff
Stream
Land surface/vegetation
Shallow
Subsurface flow
Drainage
Groundwater
Baseflow

Figure 5.1 Conceptual model of the fate and transport of organochlorines in an alpine catchments. The boxes represent storage reservoirs for OCs, and the ovals represent processes governing the transfer and partitioning between reservoirs. The varying thickness of the arrows illustrates the approximate relative magnitude of transfers between reservoirs.

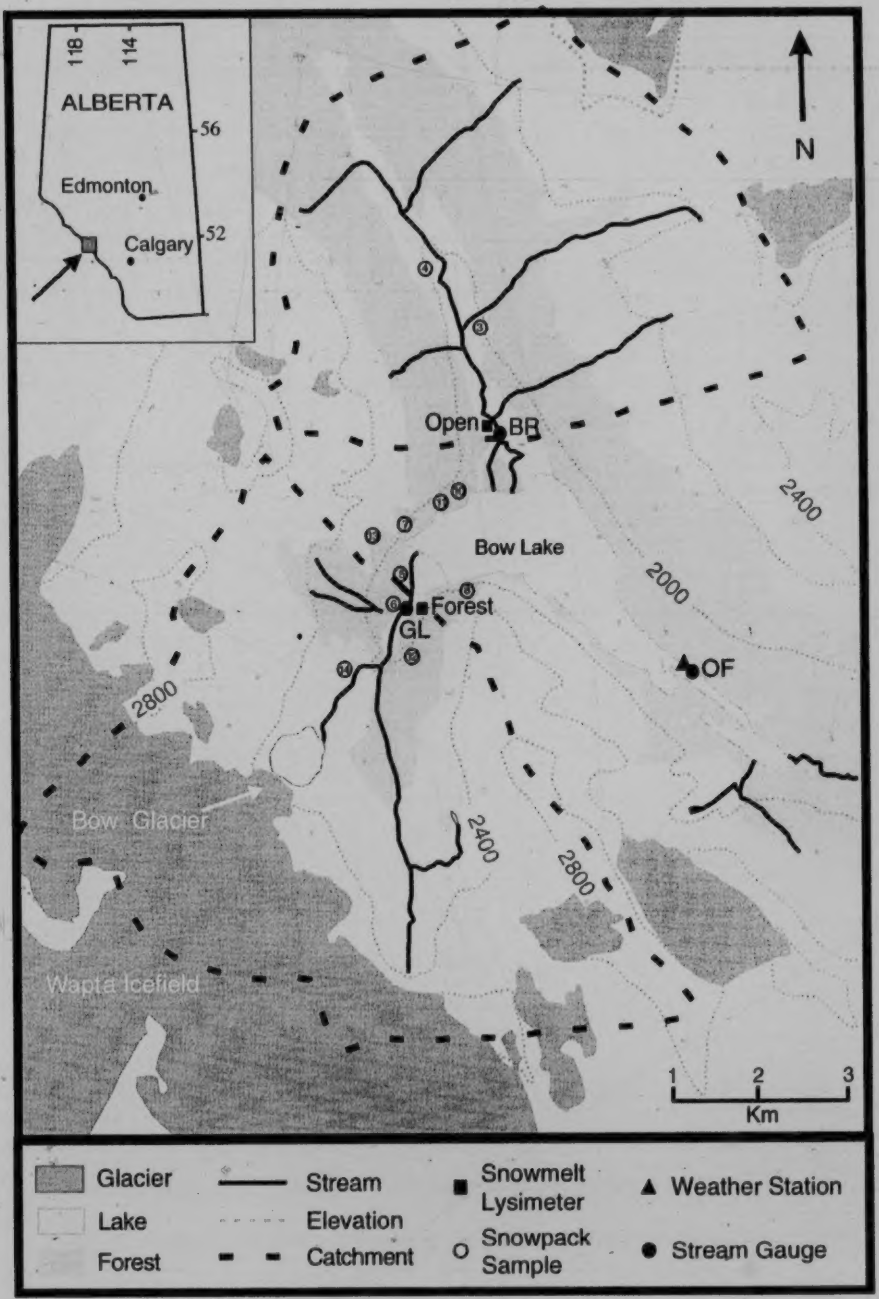
118
114
ALBERTA
56
52
Edmonton
Calgary
N
Open
BR
Bow Lake
Forest
GL
OF
2400
2000
2800
2800
2400
2800
Bow Glacier
Wapta Icefield
1
2
3
Km
Glacier
Lake
Forest
Stream
Elevation
Catchment
Snowmelt Lysimeter
Snowpack Sample
Weather Station
Stream Gauge

Figure 5.2 Map of Bow Lake catchment illustrating the location of the weather station, snowmelt lysimeters, snowpack sampling sites, as well as the stream gauging station and sampling sites.

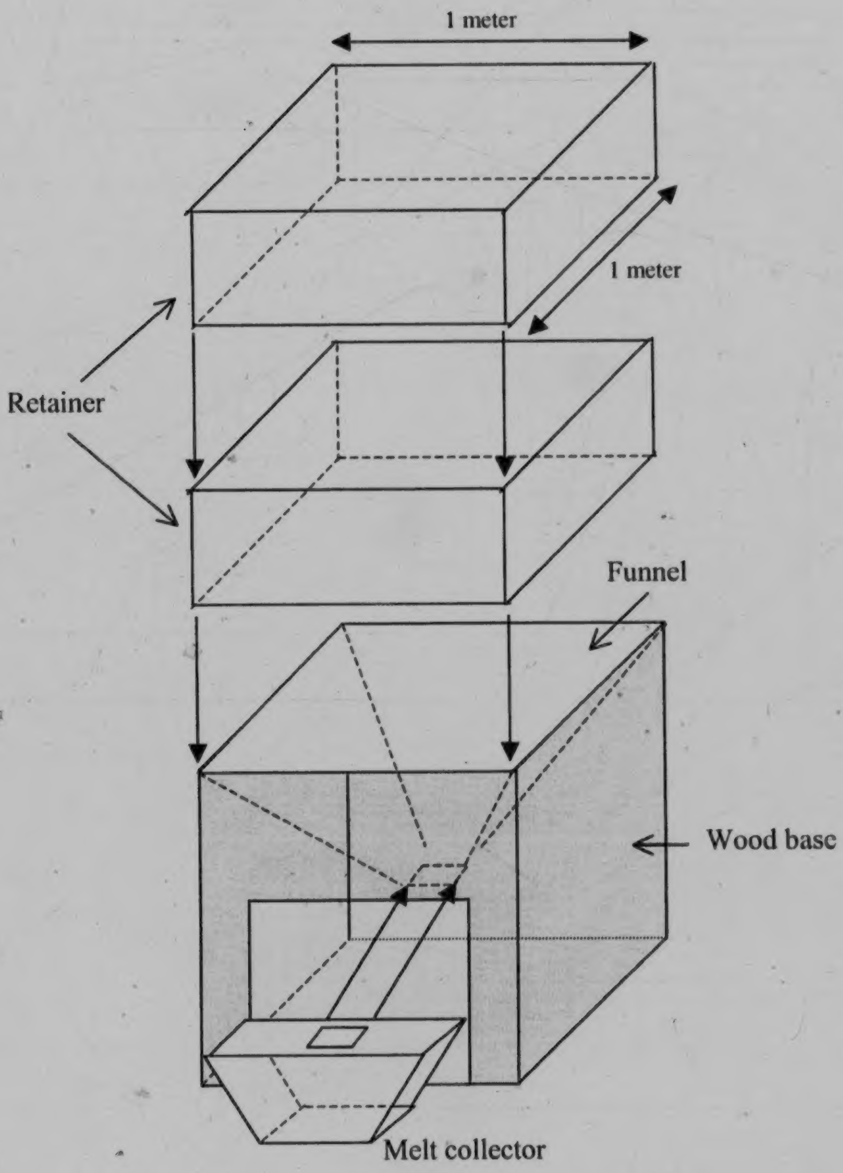
1 meter
1 meter
Retainer
Funnel
Wood base
Melt collector

Figure 5.3 Diagram of the snowmelt lysimeter apparatus

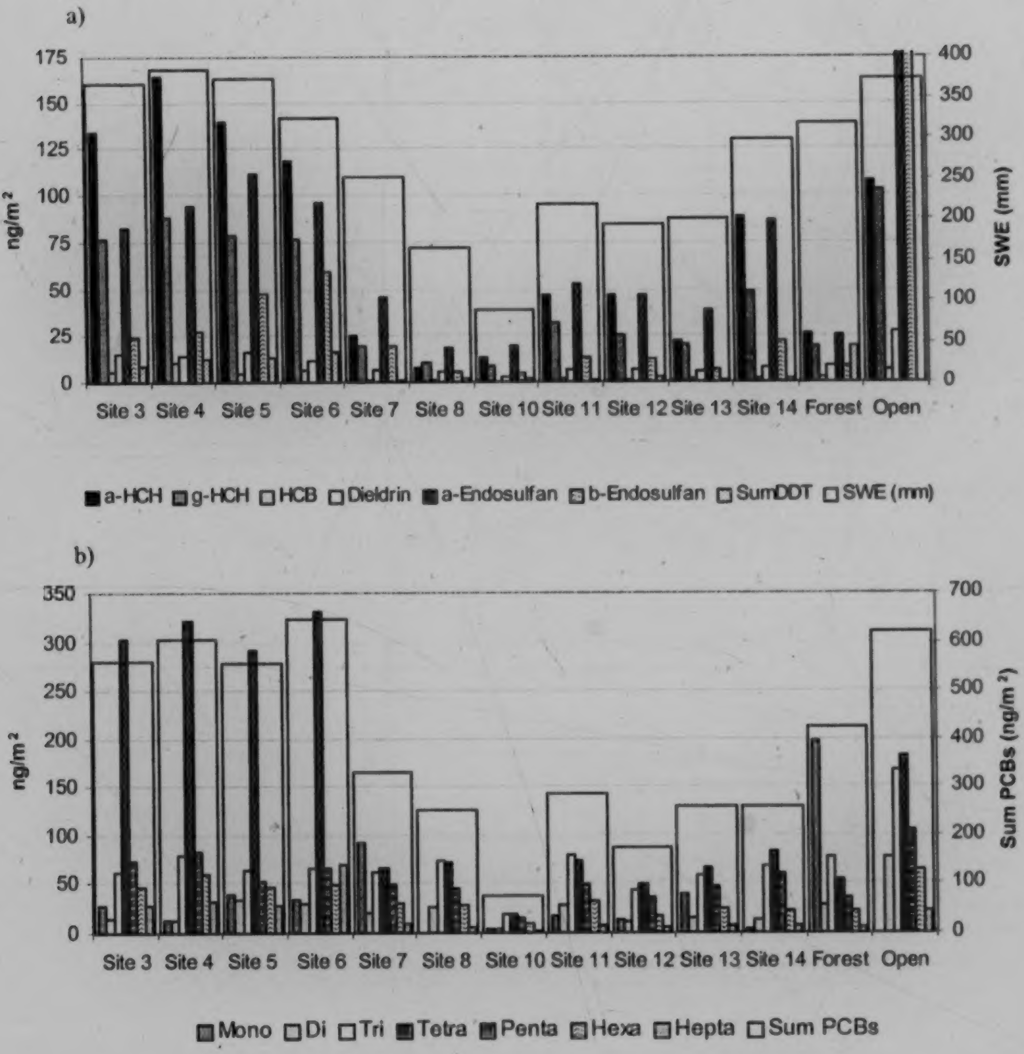

Figure 5.4 Snowpack OC burdens (ng/m^2). (a) OC pesticide burdens (left axis) and snowpack SWE (right axis) (b) Snowpack burdens for PCB homologue groups (left axis) and total PCBs (right axis). Figure 2 shows the location of each site.

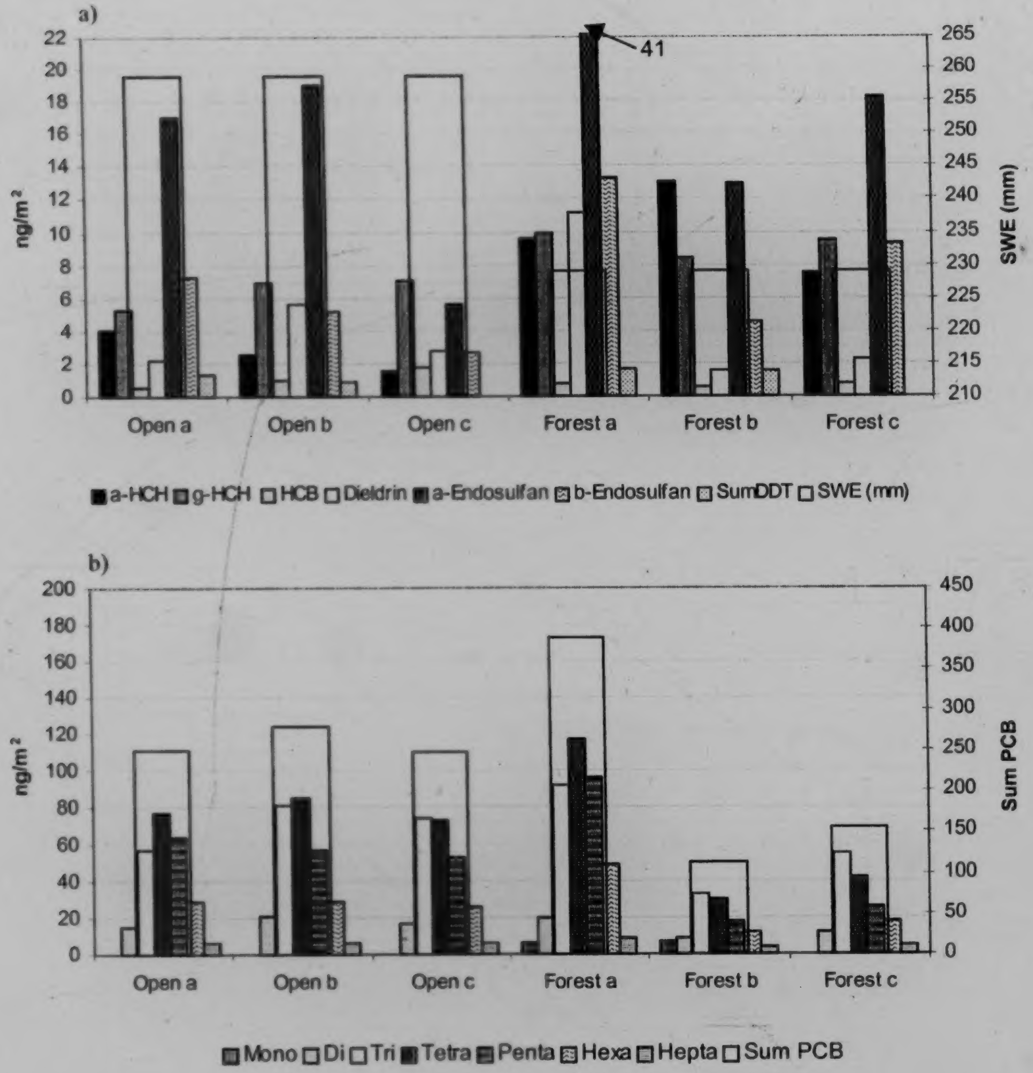

Figure 5.5 Snowpack OC burdens for the Forest and Open lysimeter sites March 25th, 1998. The letters a, b, and c designate replicate samples (a) OC pesticides and snowpack (SWE), (b) PCBs by homologue groups

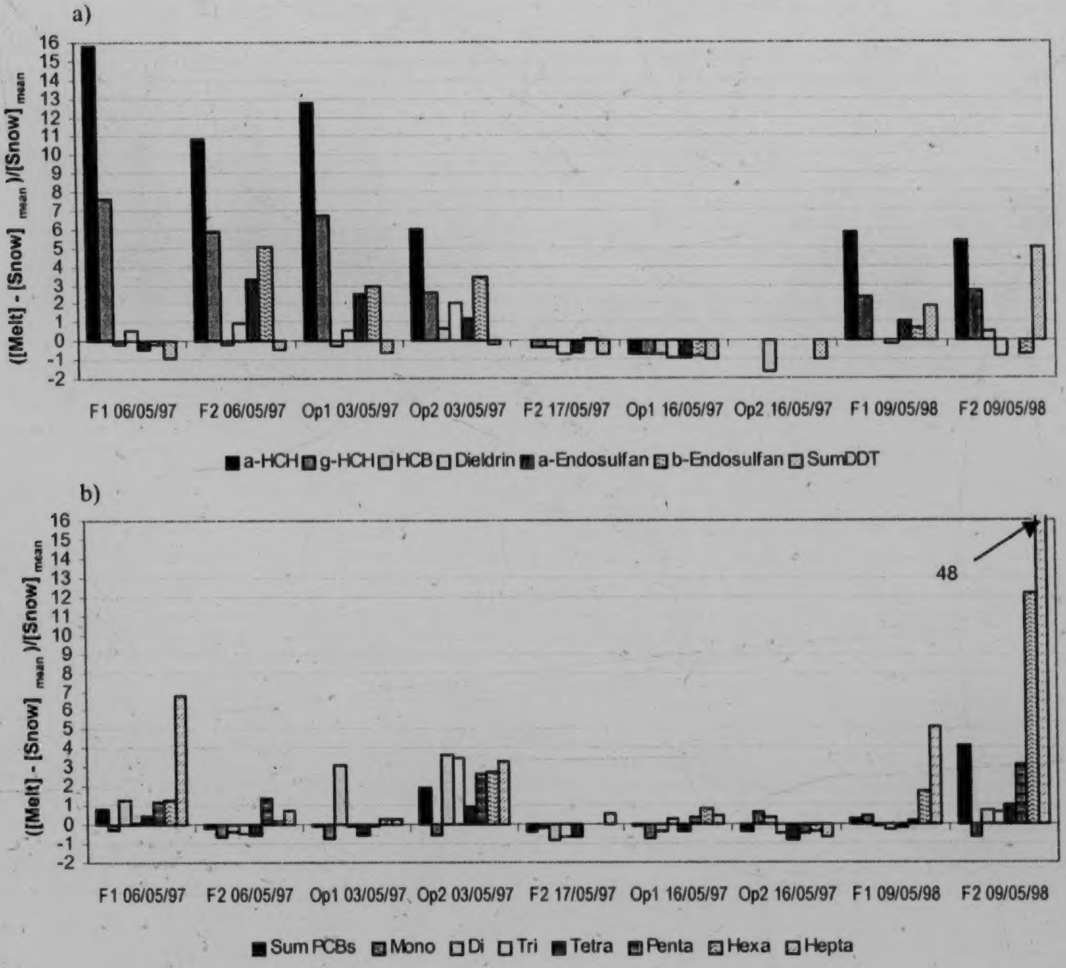

Figure 5.6 Enrichment of OC concentrations in snowmelt relative to the average winter snowpack concentration: ([Melt]-[Snow]$_{mean}$)/SD([Snow]$_{mean}$) (a) OC pesticides and snowpack (SWE); (b) PCB burdens by homologue groups

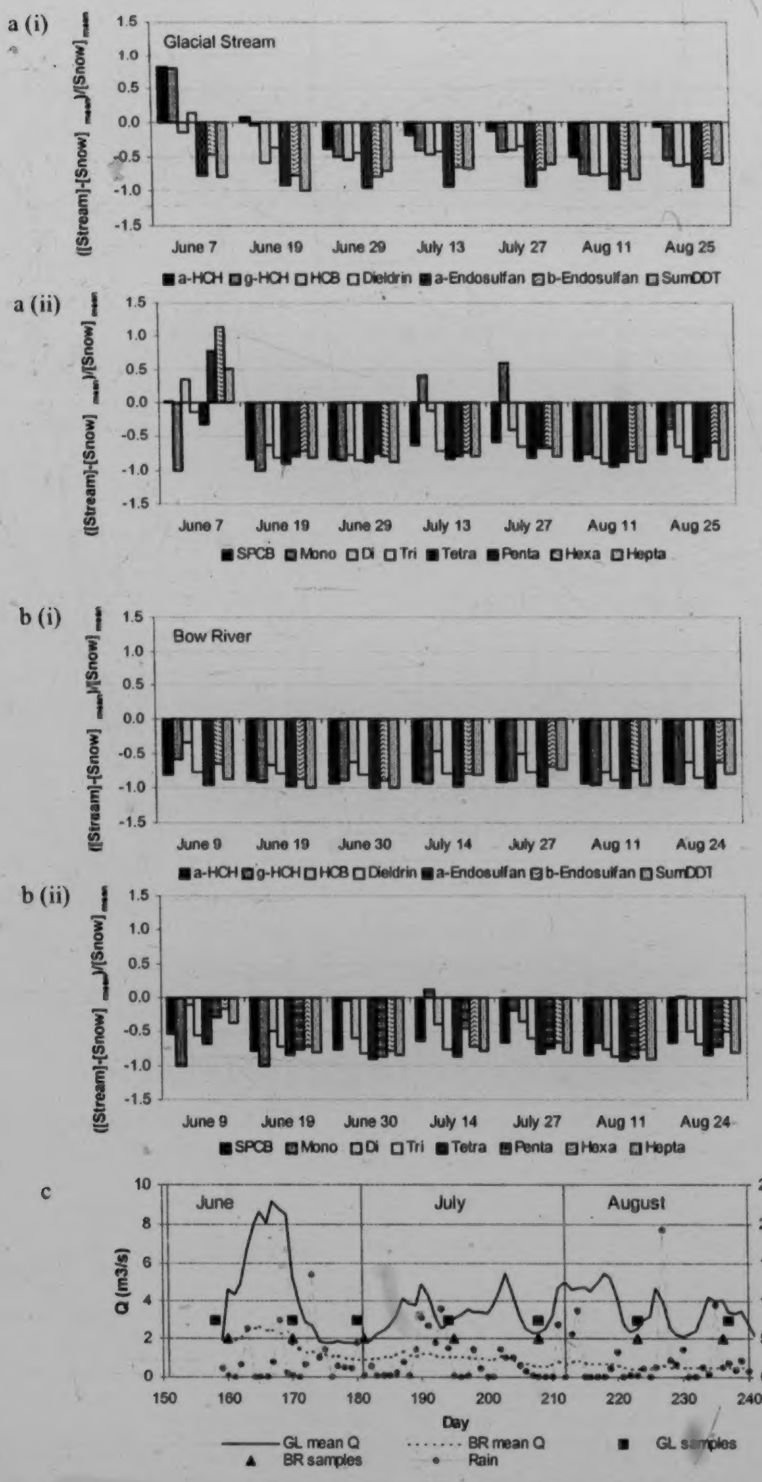

Figure 5.7 Enrichment of OC concentrations in runoff (([Stream]-[Snow]mean)/[Snow]mean) in 1997 for (a) the Glacial stream and (b) the Bow River: (i) OC pesticides and (ii) PCBs; (c) the stream discharges and sampling times

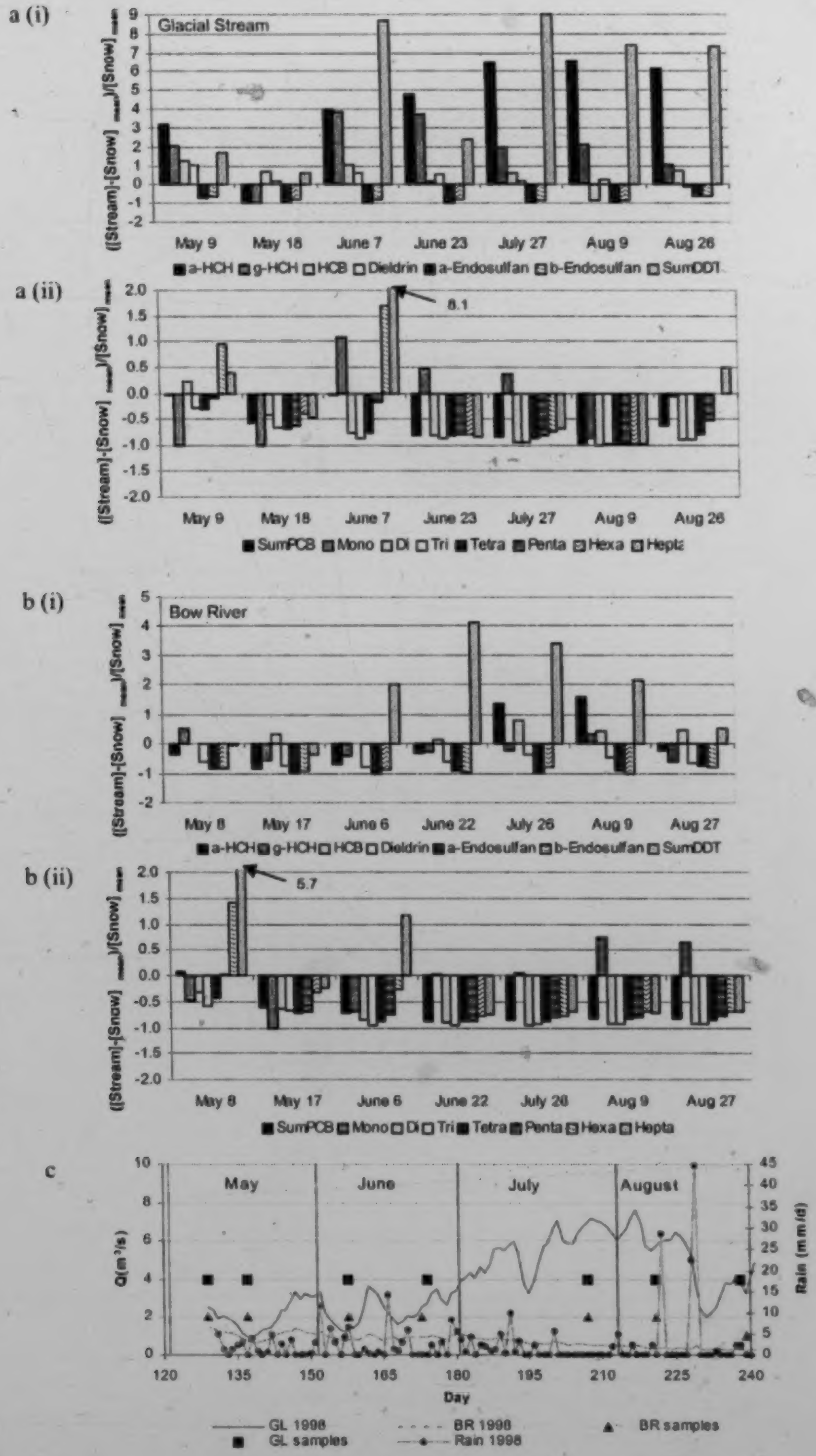

Figure 5.8 Enrichment of OC concentrations in runoff (([Stream]-[Snow]mean)/[Snow]mean) in 1998. (a) the Glacial stream and (b) the Bow River: (i) OC pesticides and (ii) PCBs; (c) the stream discharges and sampling times

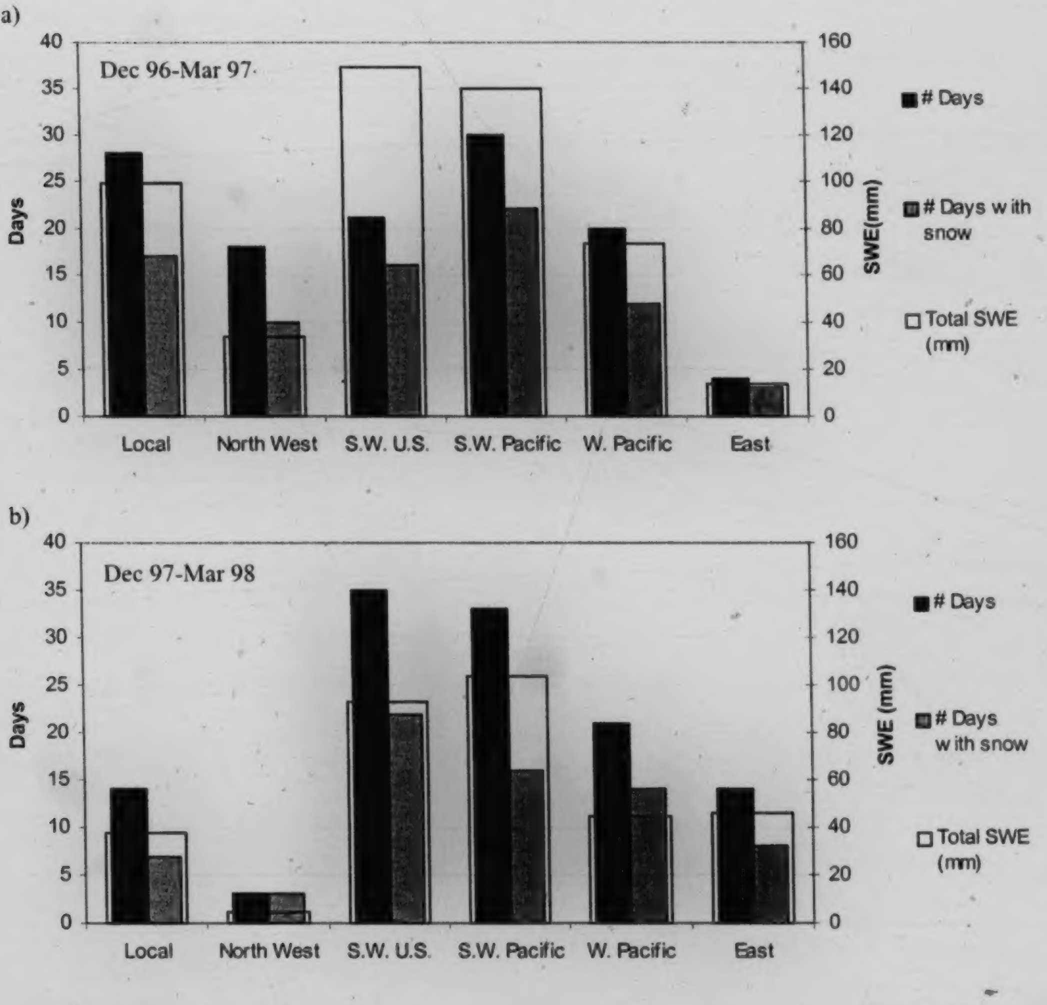

Figure 5.9 Origin of air masses (5 day back trajectories) for December-March (a) 1996/1997 and (b) 1997/1998. ' # Days' is the number of days between Dec-Mar when the air mass originated from a given area, ' # Days with snow' is the number of days that air mass originating from a given source area also resulted in snowfall at the Sunshine Village snow pillow site. Total SWE, is the total amount of snow (SWE mm) that fell at Sunshine Village for air masses originating from each area. The Local area includes B.C. and Alberta (45-60° N, 110-130° W), the North West includes the area north of 60° and west of 110° W, S.W. U.S. includes the area south of 45°N, and between 110-130° W., S.W. Pacific includes all areas south of 45°N and west of 130° W, W. Pacific is the area between 45-60°N and west of 130°W, and the East includes all latitudes east of 110°W.

Chapter 6: Summary and Conclusions

6.1 SUMMARY

This research (a) enhances our knowledge of the hydrological and biogeochemical processes of glacial and non-glacial environments (b) demonstrates that glacial and non-glacial catchments draining into Bow Lake experience opposite discharge and solute flux responses to ENSO forcing, (c) describes the nature and origin of DOC in glacial runoff and how these characteristics differ from those in snowmelt fed catchments, (d) demonstrates that the flux of OCs in glacial runoff is not simply a function of the OC burden in the previous winter's snowpack, and (e) raises questions about the importance of forests, glacial ablation, and inter-annual storage of OCs in ice and firn for the flux of OCs in catchment runoff

The results of Lafrenière and Sharp (2003) (Chapter 2) show that glacial and non-glacial catchments exhibit opposite discharge responses to ENSO forcing. Several studies of streamflow response to atmospheric forcing have shown that rivers on the west coast of Canada and the U.S.A. typically experience lower stream flows in the year following the onset of El Niño (Kahya and Dracup, 1993; Kiladis and Diaz, 1989; Redmond and Koch, 1991). This study indicates that although the early disappearance of snow from the catchments and elevated air temperature in 1998 resulted in low seasonal discharge in the snowmelt-fed Bow River, the 1998 El Niño conditions led to substantially higher discharges in the Glacial stream. Significant ice exposure and the development of channelised glacial drainage are inferred in late summer 1998, and moderate ice exposure (but no obvious development of channelised subglacial drainage) in 1997. Snowmelt was the dominant runoff source in the two streams in 1999 and 2000, and to a lesser extent in 1997. The analyses enabled the identification of a small area of ice cover in the Bow River catchment and showed that its contribution to diurnal variations in late summer runoff can be significant when the retreat of the snowpack is relatively early, even though the ice covers no more than 1-2% of the Bow River catchment. This paper illustrates that wavelet analysis is an efficient and effective method for continuous and quantitative spectral analysis of large hydroclimatological data sets. The method identifies inter-annual and seasonal changes in the contributions of different water sources to runoff and general changes in catchment flow routing, and does not require the extensive data preparation associated with other time series techniques (Gurnell et al., 1992; Hodgkins, 2001).

Chapter 3 indicates that runoff in the Bow River has more contact with terrestrial sources of organic carbon than runoff in the Glacial catchment. Although previous studies have documented the behaviour and spectrofluorometric properties of DOC in alpine streams and lakes, and Antarctic lakes (Boyer et al., 1997; Curtis and Adams, 1995; Donahue et al., 1998; McKnight et al., 1994; McKnight et al., 2001), to our knowledge this paper is the first to examine the concentration and quality of DOC in glacial runoff, and to compare the seasonal variations in these parameters in runoff from adjacent glacial and non-glacial catchments. It was determined that the DOC in the Bow River originates from soil and plant organic matter that is flushed to the stream by shallow subsurface flow during snowmelt, and that the flow routing and source of DOC in this catchment did not vary appreciably from year to year, despite significant inter-annual variations in snowpack volume. As for early season snowmelt runoff, rainfall was observed to flush terrestrial DOC from the shallow subsurface to the stream. In the Glacial stream, the abundance of terrestrially derived DOC was very limited compared to the non-glacial catchment. It is thought that the microbial nature of DOC in the Glacial stream could be the result of microbial and algal activity in snow, on the glacier surface, or in subglacial environments (Sharp et al., 1999; Skidmore et al., 2000). However, further examination of DOC from glacial systems in late summer, with better temporal resolution, is necessary to better constrain the range of concentrations and the controls on the characteristics of DOC from subglacial environments.

Chapter 4 demonstrates that adjacent glacial and non-glacial catchments experienced opposite solute flux responses to climate perturbations. El Niño conditions (low winter snowfall and warm spring and summer air temperatures) led to increases in the flux of solutes from the glacial catchment, and decreases in the solute flux from the snowmelt fed catchment, relative to La Niña conditions. Inter-catchment differences in solute composition were primarily controlled by differences in catchment geology and the presence of soils, while differences in total solute fluxes were largely dependant on specific discharge. The Glacial stream had higher chemical denudation rates due to the high rates of flushing (high specific discharge). The Bow River had higher overall concentration of solutes despite the greater presence of more resistant lithologies, indicating that runoff likely has longer residence time (i.e. greater water:rock contact time). Increases in snowpack depth/snowmelt runoff in the non-glacial Bow River reduced the retention of nitrate in this catchment (i.e. increased nitrate export), probably by reducing net biological uptake, or by reducing the proportion of runoff that has contact with biologically active soil horizons that tend to remove nitrate. In the Bow River seasonal solute fluxes increased proportionally with discharge, indicating that increased supply of snowmelt runoff results in a proportional increase in weathering rates. In contrast, the increase in solute flux in the Glacial stream was less than (~70-80%) the increase in water flux. The solute chemistry suggests increases in glacial ablation and the development of subglacial channels during the 1998 El Nino year reduced the average water:rock contact time in the glacial catchment relative to seasons when the subglacial drainage system was primarily distributed (Lafrenière and Sharp, 2003).

In Chapter 5 it was determined that the concentration of OCs in the snowpack in a given year can vary substantially over relatively small distances. The presence of forests appears to reduce the total accumulation and increase volatilization losses of snow and contaminants. Forests might therefore contribute to the observed increase in contaminant deposition with elevation (Blais et al., 1998), since forest cover decreases with increasing elevation. Inter-annual differences in snowpack OC burdens appear to be due to the combination of more precipitation from air masses originating from the S.W. Pacific and S.W. U.S., higher total snow accumulation and accumulation rates, and lower air temperatures in 1997 than in 1998. The degree of enrichment of a compound in snowmelt relative to snow was strongly related to the aqueous solubility and octanol-water partitioning coefficient of the chemical. In the streams, OCs were only enriched relative to the winter snow during snowmelt and in late summer 1998 when there was significant exposure of glacial ice. The significant enrichments in the Glacial runoff and little or no enrichment in the Bow River during snowmelt, are probably largely due to the higher sorption of OCs to soils or vegetation during the routing of melt water in the Bow River catchment. The extent of glacial ablation appears to be an important control on the flux of OCs to the lake in 1998. The similarity in the OC concentrations in the Bow River between 1997 and 1998, suggest that in this catchment, retention captures such a large proportion of available OCs, that the original the snowpack burden may have little effect on the flux of OCs to the streams.

6.2 IMPLICATIONS FOR OC TRANSPORT AND FUTURE RESEARCH

This research indicates that there are many aspects of glacial catchments that will enhance the delivery of OCs to the lake via runoff, relative to non-glacial environments.

The DOC analyses and solute chemistry show that runoff from the glacial catchment has less contact with organic soils than runoff from the snowmelt-fed catchment, where OCs in snowmelt runoff have ample opportunity to sorb to organic matter when snowmelt infiltrates the soils during the early stages of snowmelt. This is likely the cause of the low OC concentrations in the Bow River relative to the concentrations in catchment snows and in the Glacial stream.

However, some of the difference may be due to lower average snowpack OC concentrations in the Bow River catchment, as a result of the larger forest covered area (Chapter 5). Results from Braekevelt (2001) indicate that 1.5ppm DOC can significantly reduce the uptake (bioconcentration) of OCs by zooplankton, due to the sorption of OCs to DOC. The sorption of OCs to DOC also increases with increasing aromaticity of the DOC (Chiou et al., 1986; Chiou et al., 1983). Therefore, the lower concentrations and less aromatic (more microbial) nature of DOC in glacial runoff (Chapter 3) should enhance the proportion of freely dissolved (hence bioavailable) contaminants relative to catchments where the flushing of soils during snowmelt provides higher concentrations of more aromatic DOC. Since the highest DOC concentrations also likely occur at the same time as the highest OC concentrations (i.e. during snowmelt runoff), the timing of the DOC pulse may also be an important factor in determining the flux of bioavailable OCs from snowmelt fed alpine catchments. The relationship between the timing of the high dissolved OC fluxes from glacial runoff and the critical time of growth and reproduction of aquatic organisms may be worth further study. A study of OC uptake by organic soils during the snowmelt period, and the re-volatilization of OCs from soils later in the season would also improve our understanding of the ultimate fate of OCs in the seasonally snow-covered catchments.

The magnitude of variability observed in OC concentrations in snows across the Bow Lake catchment in 1997 is comparable to the variability observed in snow samples taken from sites across arctic Canada (Gregor and Gummer, 1989; Macdonald et al., 2000). This observation suggests that, ideally, studies of OC contamination in snow should include a careful description of the physical structure of the snowpack and measurements of the DOC/POC content for each sample in order to fully explain the content and distribution of OCs within the snowpack. Multiple samples would also impart greater confidence to results, especially for studies in forested areas, where the variability in OC concentrations from replicate samples were substantial. Further research on the impact of vegetation/forests on OC deposition/volatilization in alpine environments is also warranted. Since, the extent of forests is usually well known and easy to map digitally, it should be relatively easy to incorporate this variable into predictive models to determine areas at risk of OC contamination

The relatively high concentrations in the first snowmelt fractions (Chapter 5 Table 5.9) and the apparent lack of correlation between vapour pressures or H constants (air-water partitioning coefficients) and the enrichment of a contaminants in snowmelt samples suggest that volatilization losses of contaminants from the snowpack were not very significant at these sites.

Studies from snow in the accumulation zone of glaciers report volatilization losses of 60-100% for most OCs within 6 months to a year of deposition (Donald et al., 1999; Franz et al., 1997). This work indicates that volatilization losses from seasonal snowpacks (when snow accumulates and melts within approximately 6 months) may not be as significant as those observed at sites where the snow does not melt completely. More measurements of the fate of OCs in the snowpack are necessary, especially to determine the proportion of contaminants that are evaporated, sorbed to POC, and leached with melt water.

The inter-annual differences in contaminant concentrations in glacial runoff did not reflect the large inter-annual differences in the snowpack OC burdens at the end of winter. The enrichment of OCs in the glacial stream relative to snowpack OCs increased with increasing inputs of glacially derived meltwater in 1998 (Chapter 2, Chapter 5). It appears that the firn aquifer and/or glacier ice (formed since approximately 1950) may be sources of OCs that were deposited as snow the preceding year, or decades before. The high enrichment of OCs with high glacial ablation may be due in part to the faster flow routing (shorter water:rock contact time), which reduces the potential for OC retention in the glacier when a channelised drainage system develops within the glacier, relative to years with primarily distributed subglacial drainage. However, the low DOC concentrations in glacial runoff all times in late summer (Chapter 3), suggest that glacial runoff probably has little contact with organic matter regardless of flow routing in the glacial/subglacial environment. Thus, the increases in OC concentrations later in the summer are likely primarily the result of increasing firn and ice melt.

This finding raises several questions: (1) How do OC fluxes vary with snowpack burden and glacial ablation? (2) To what extent do antecedent conditions (i.e. deposition and flushing of OCs from the snow/firn aquifer and the glacier the previous year) control annual OC fluxes? The results from Blais et al (2000b) indicate that the fluxes of some contaminants from the glacial catchment were greater in 1998 than 1997. Therefore, lower snowfalls (and snowpack OC burdens) and higher glacial ablation (i.e. El Niño conditions) can result in higher annual OC fluxes than occur in years when annual snow accumulation and OC burden are higher.

The results of this thesis suggest that future research should focus on the OC dynamics during snowmelt and late summer glacial melt. This should involve high frequency sampling of the snowpack, the firn aquifer, and ice surface runoff during peak summer flows to determine if these waters are contaminated. Also, frequent measurements of the physical characteristics of the snowpack (to record the progress of metamorphism and melting), and measurements of glacial ablation, would help determine the extent to which the snowpack and glacial ice OC burdens control the OC load delivered to the lake in glacial runoff. The nature of the flow routing on and within glaciers should also be considered, to better define the impact of channelised flow routing on the volatilization and sorption of OCs.

Previous studies at Bow Lake determined that glacier ice melt was an important contributor of persistent organic pollutants to surface waters (Blais et al., 2001a; Blais et al., 2001b). This study suggests that snow, firn, and ice melt are all likely important sources of OCs to glacial runoff. Furthermore, this work indicates that a combination of low forest and soil cover in the glacial catchment, and lower DOC concentrations in runoff likely contribute to high deposition, efficient delivery, and high bioavailability of OCs in glacial runoff. Future research should focus on better temporal resolution of the OC fluxes during snowmelt and glacial melt periods, and the relative importance of volatilization and leaching of OCs from snow in both forested and barren alpine terrain.

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Appendices

a)

	Start	End	Start	End	BL=m*BS+b	R2	N	Significance Level %	Standard Error (b)	Standard Error (m)
	Calendar		Julian Day							
1997	Aug 10, 18:00	Aug 20, 19:00	222.75	232.79	BL=0.93*BS+1.81	0.88	291	99.99	0.22	0.03
	Aug 21, 12:00	Aug 24, 17:00	233.50	236.71	same as above					
	Aug 26, 10:00	Aug 31, 24:00	238.42	244.00	same as above					
1998	June 16, 1:00	June 27, 23:00	167.04	178.96	BL=0.91*BS+1.63	0.82	288	99.99	0.22	0.03
	July 20, 2:00	July 28, 20:00	201.08	209.83	BL=0.84*BS+2.52	0.74	530	99.99	0.25	0.02
	Aug 9, 12:00	Aug 20, 11:00	221.50	232.46	BL=0.67*BS+4.54	0.74	230	99.99	0.35	0.03
	Aug 22, 15:00	Sept 4, 11:00	234.64	247.46	same as above					

b)

	Start	End	Start	End	BL=m*BS+b	R2	N	Significance Level	Standard Error (b)	Standard Error (m)
	Calendar		Julian Day							
Temperature										
1997	Aug 10	Aug 24	222.00	236.00	BL=0.89*BS+1.50	0.95	67	99.99	0.22	0.03
	Aug 26	Aug 31	238.00	244.00	same as above					
1998	June 16	June 27	167.00	178.00	BL=0.92*BS+1.54	0.95	52	99.99	0.29	0.03
	July 20	July 28	201.00	209.00	same as above					
	Aug 9	Aug 20	221.00	232.00	same as above					
	Aug 22	Sept 4	234.00	247.00	same as above					
Precipitation										
1997	Aug 10	Aug 24	222.00	236.00	BL=0.79*BS+0.012	0.90	61	99.99	0.13	0.03
	Aug 26	Aug 31	238.00	244.00	same as above					
1998	June 16	June 27	167.00	178.00	BL=2.19*BS+0.162	0.80	67	99.99	0.17	0.14
	July 20	July 28	201.00	209.00	same as above					
	Aug 9	Aug 20	221.00	232.00	same as above					
	Aug 22	Sept 4	234.00	247.00	same as above					

Appendix 1 Regression equations and statistics for gaps in the temperature and precipitation records at the Bow Lake (BL) meterological station using the record from Bow Summit (BS) (a) regressions for hourly temperature records. (b) regressions for daily mean temperature and precipitation records.

Stream	Year	Solute	Days	Regression Equation	R^2	N	OL	SE	$p <$
Bow River	1998	Na^+	128-203	$Na^+ = -9.25*Q + 36.64$	0.81	15	5	1.04	0.00000
			208-275	$Na^+ = -30.60*Q + 39.05$	0.78	12	0	2.44	0.00014
		K^+	128-218	$K^+ = 1.68*Q + 6.36$	0.62	20	4	0.27	0.00003
			220-275	$K^+ = -7.00*Q + 11.20$	0.80	8	0	0.36	0.00027
		Mg^{2+}	128-203	$Mg^{2+} = -248.0*Q + 1225$	0.84	18	2	23.2	0.00000
			208-275	$Mg^{2+} = -1127*Q + 1526$	0.82	12	0	82.6	0.00005
		Ca^{2+}	128-203	$Ca^{2+} = -254.3*Q + 1476$	0.75	18	2	31.6	0.00000
			208-275	$Ca^{2+} = -784.3*Q + 1653$	0.69	12	0	79.9	0.00056
		Sr^{2+}	128-275	$Sr^{2+} = -0.97*Q + 3.28$	0.36	31	1	0.39	0.00039
		Cl^-	128-275	$Cl^- = 3.29*Q + 4.21$	0.72	22	10	0.72	0.00000
		NO_3^-	128-275	$NO_3^- = -1.93*Q + 2.41$	0.73	31	1	0.91	0.00260
		SO_4^{2-}	128-275	$\log SO_4^{2-} = -0.533*\log Q + 2.40$	0.81	31	1	1.13	0.00000
		HCO_3^-	128-203	$\log HCO_3^- = -0.154*\log Q + 3.29$	0.54	19	1	1.44	0.00032
			208-275	$\log HCO_3^- = -0.234*\log Q + 3.20$	0.72	12	0	1.06	0.00045
Bow River	1999	Na^+	145-291	$\log Na^+ = -0.565*\log Q + 1.52$	0.95	19	1	1.12	0.00000
		K^+	145-291	$\log K^+ = -0.0101*\log Q + 0.902$	0.80	21	0	0.45	0.00000
		Mg^{2+}	145-291	$\log Mg^{2+} = -0.211*\log Q + 3.01$	0.99	17	3	35.9	0.00000
		Ca^{2+}	145-291	$\log Ca^{2+} = -0.179*\log Q + 3.10$	0.94	20	0	57	0.00000
		Sr^{2+}	145-291	$Sr^{2+} = -0.467*Q + 2.64$	0.66	11	8	0.26	0.00230
		Cl^-	145-291	$\log Cl^- = -1.12*\log Q + 1.12$	0.92	16	0	1.33	0.00000
			208-291	$\log Cl^- = -0.604*\log Q + 0.556$	0.99	4	0	1	0.00010
		NO_3^-	145-291	$NO_3^- = -1.80*Q + 0.178$	0.54	18	2	1.12	0.00053
		SO_4^{2-}	145-194	$\log SO_4^{2-} = -0.508*\log Q + 2.84$	0.60	13	0	1.16	0.00134
			194-291	$SO_4^{2-} = -208.4*Q + 604.5$	0.81	7	0	44.6	0.00547
		HCO_3^-	145-291	$\log HCO_3^- = -0.180*\log Q + 3.31$	0.87	19	1	65.9	0.00000
Bow River	2000	Na^+	123-208	$\log Na^+ = -0.577*\log Q + 1.47$	0.94	28	0	1.09	0.00000
		K^+	123-208	$K^+ = -1.40*Q + 9.145$	0.66	24	4	0.3	0.00000
		Mg^{2+}	123-208	$Mg^{2+} = -328.6*Q + 1318$	0.97	26	2	20.3	0.00000
		Ca^{2+}	123-208	$Ca^{2+} = -402.4*Q + 1659$	0.89	26	2	44.6	0.00000
		Sr^{2+}	123-208	no regression, mean Sr =1.89		18	10	0.27	
		Cl^-	123-208	$\log Cl^- = -1.38*\log Q + 0.902$	0.91	28	0	1.27	0.00000
		NO_3^-	123-208	$NO_3^- = -2.47*Q + 5.47$	0.92	23	5	0.22	0.00000
		SO_4^{2-}	123-187	$\log SO_4^{2-} = -0.303*\log Q + 2.259$	0.82	24	0	1.07	0.00000
			187-208	$SO_4^{2-} = -208.4*Q + 604.5$	0.81	7	0	44.6	0.00547
		HCO_3^-	123-208	$HCO_3^- = -650.1*Q + 2752$	0.96	23	5	43.6	0.00000

Appendix 2 Regression equations and statistics for ion concentrations (dependent variable) and discharge (independent) for the Bow River 1998-2000. N is the number of samples used to obtain the regression, OL is the number of samples that were considered outliers, SE is the standard error on the estimate, and p is the significance of the regression.

Stream	Year	Solute	Days	Regression Equation	R^2	N	OL	SE	$p <$
Glacial	1998	Na^{+}	135-276	$Na^{+} = -0.774*Q + 11.62$	0.66	33	1	1.17	0.00000
		K^{+}	135-276	$K^{+} = -0.227*Q + 4.87$	0.41	31	3	0.58	0.00012
		Mg^{2+}	135-276	$\log Mg^{2+} = -0.385*\log Q + 2.86$	0.67	34	0	1.17	0.00000
		Ca^{2+}	135-276	$\log Ca^{2+} = -0.151*\log Q + 3.02$	0.68	29	5	1.06	0.00000
		Sr^{2+}	135-276	$Sr^{2+} = -1.08*Q + 13.52$	0.89	29	5	0.76	0.00000
		Cl^{-}	135-276	$\log Cl^{-} = -0.446*\log Q + 0.491$	0.73	22	9	0.06	0.00000
		NO_3^{-}	135-276	$NO_3^{-} = -0.977*Q + 8.69$	0.80	25	6	0.91	0.00260
		SO_4^{2-}	135-276	$SO_4^{2-} = -32.00*Q + 384.8$	0.86	29	2	26.9	0.00000
		HCO_3^{-}	135-276	$\log HCO_3^{-} = -0.245*\log Q + 3.16$	0.84	24	3	1.06	0.00000
Glacial	1999	Na^{+}	147-291	$\log Na^{+} = -0.237*\log Q + 1.12$	0.85	18	7	1.07	0.00000
		K^{+}	147-291	$K^{+} = -0.567*Q + 6.69$	0.73	21	6	0.38	0.00000
		Mg^{2+}	147-291	$Mg^{2+} = -152.2*\log Q + 1150$	0.64	23	2	130	0.00000
		Ca^{2+}	147-291	$Ca^{2+} = -136.7*Q + 1470$	0.50	23	2	153	0.00005
		Sr^{2+}	147-291	$\log Sr^{2+} = -0.221*\log Q + 1.11$	0.88	23	2	1.09	0.00000
		Cl^{-}	147-291	$\log Cl^{-} = -0.272*\log Q + 0.657$	0.67	20	7	1.21	0.00001
		NO_3^{-}	147-291	$NO_3^{-} = -0.897*Q + 9.48$	0.54	23	4	0.91	0.00006
		SO_4^{2-}	147-291	$\log SO_4^{2-} = -0.332*\log Q + 2.67$	0.92	23	4	1.11	0.00000
		HCO_3^{-}	147-291	$HCO_3^{-} = -141.1*Q + 1904$	0.50	25	2	180	0.00008
Glacial	2000	Na^{+}	123-208	$Na^{+} = -1.84*Q + 16.70$	0.94	26	6	0.71	0.00000
		K^{+}	123-208	$K^{+} = -0.757*Q + 6.97$	0.94	29	3	0.28	0.00000
		Mg^{2+}	123-208	$Mg^{2+} = -164.3*Q + 1170$	0.96	28	4	20.3	0.00000
		Ca^{2+}	123-208	$Ca^{2+} = -148.6*Q + 1455$	0.91	28	4	67.4	0.00000
		Sr^{2+}	123-208	$Sr^{2+} = -1.29*Q + 15.13$	0.74	30	2	1.18	0.00000
		Cl^{-}	123-208	$\log Cl^{-} = -1.00*Q + 6.08$	0.93	20	11	0.45	0.00000
		NO_3^{-}	123-208	$NO_3^{-} = -0.835*Q + 9.87$	0.98	25	6	0.22	0.00000
		SO_4^{2-}	123-208	$SO_4^{2-} = -69.34*Q + 581.3$	0.80	29	2	54.5	0.00000
		HCO_3^{-}	123-208	$HCO_3^{-} = -230.6*Q + 2038$	0.93	30	1	87.2	0.00000

Appendix 3 Regression equations and statistics for ion concentrations (dependent variable) and discharge (independent) for the Glacial stream 1998-2000. N is the number of samples used to obtain the regression, OL is the number of samples that were considered outliers, SE is the standard error on the estimate, and p is the significance of the regression.

Site	Sample Name	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	T°C (of pH)	EC (μS/cm)
BR	I060697	157.00	13.0	7.21	4.0	354	428	0.0	5.3	3.4	117				
BR	I062097	171.00							6.3	1.1	176				
BR	I062797	178.00	27.8	0.00	6.8	895	1159	0.0	6.3	1.7	202				
BR	I070497	185.00	61.5	4.18	7.1	763	958	0.0	6.7	2.1	299				
BR	I071197	192.00	44.1	1.03	7.4	829	1061	0.0	13.2	0.0	235				
BR	I07159710	196.42							3.7	1.0	184	1576	8.28	5.5	
BR	I07159712	196.50	23.6	1.59	6.7	839	1078	0.0	4.6	1.0	233	1584	8.36	7.3	
BR	I07159714	196.58	24.0	0.83	7.0	848	1088	0.0	4.5	0.9	236	1658	8.35	8.3	
BR	I07159716	196.67	24.6	1.54	7.3	857	1102	0.0	4.5	0.7	238	1610	8.36	9.5	
BR	I07229710	203.42	21.3	0.81	7.2	763	998	0.0	5.4	0.9	194		8.22	6.1	120
BR	I07229712	203.50	20.0	0.00	6.2	775	1009	0.0	3.7	0.8	212	1488	8.18	7.5	127
BR	I07229714	203.58	20.1	1.00	6.2	750	977	0.0	3.4	0.8	216	1476	8.14	8.2	123
BR	I07229716	203.67	21.5	0.71	7.0	783	1015	0.0	3.5	0.6	217	1504	8.10	10.6	129
BR	I072897	209.00	55.0	2.03	9.2	919	1178	0.0	11.3	0.0	128			10.1	144
BR	I07289710	209.42	26.8	0.69	6.9	920	1158	0.0	4.3	0.9	270	1696	8.21	5.7	142
BR	I07289714a	209.58	27.2	4.48	7.2	923	1183	0.0	4.3	1.0	268	1688	8.30	12.4	145
BR	I07289716	209.67	26.5	1.46	7.4	879	1141	0.0	4.1	1.0	261	1684	8.30	14.3	140
BR	I081197	223.00	28.3	0.00	10.1	850	1086	0.0	6.3	1.0	298				
BR	I08149710	226.42	25.0	0.00	7.1	929	1147	0.0	5.4	1.8	313	1768	8.20	6.8	192
BR	I08149712	226.50	24.1	0.00	7.1	894	1118	0.0	4.4	1.3	293	1744	8.15	9.2	185
BR	I08149714	226.58	23.9	0.67	7.0	858	1107	0.0	4.3	1.2	288	1648	8.26	10	178
BR	I08149716	226.67	22.9	0.00	7.4	852	1093	0.0	4.0	0.9	287	1656	8.20	11	176
BR	I08199710	231.42	28.4	0.00	7.8	996	1193	0.0	8.2	2.3	360	1816	8.30	4.6	199
BR	I08199712	231.50	37.5	1.11	8.0	989	1204	0.0	6.9	1.8	356	1800	8.10	7.2	198
BR	I08199714	231.58	44.1	0.00	8.4	965	1189	0.0	6.4	1.3	348	1784	8.26	10.7	193
BR	I08199716	231.67	29.3	0.00	8.2	926	1154	0.0	6.1	1.2	335	1724	8.17	11.8	184
BR	I10049710	277.42	33.5	1.06	8.6	1073	1308	0.0	19.3	3.0	359	1872	8.09	2	180
BR	I10049715	277.62	32.5	0.00	8.5	1056	1307	0.0	9.9	1.7	359	2088	8.11	4	214
BR	I111597	319.00	40.9	0.00	8.4	1256	1488	0.0	8.2	3.6	432	2252	8.10		252

Appendix 4 1997 Stream Sample Chemistry. All concentrations in μeq/L. For sample name, first letter designates the site, numbers give the sample date (6) and time in hours (2), and suffixes (e.g. a and b) designate duplicate samples. Day is the day of the year, fractions indicate specific hour of sampling when multiple samples were collected in one day.

Site	Sample Name	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	T°C (of pH)	EC (μS/cm)
GL	L062797	178.00	8.9	4.85	4.4	571	876	10.9	2.0	4.5	286				
GL	L070497	185.00	7.0	2.09	4.0	455	765	7.4	1.3	4.2	219				
GL	L071097	191.00	25.0	0.95	4.2	427	767	6.4	3.4	4.4	241				
GL	L07149710	195.42	7.6	0.83	3.8	486	805	9.7	1.6	4.0	252	986	8.05		128
GL	L07149712	195.50	7.5	0.72	3.8	485	803	9.7	1.6	4.2	258	964	8.06		92
GL	L07149714	195.58	7.4	0.71	3.8	485	804	9.2	1.6	4.4	257	984	8.08		95
GL	L07149716	195.67	7.3	0.99	3.7	480	802	9.3	1.5	4.1	247	986	8.13		97
GL	L07219710	202.42	5.9	0.72	2.8	352	677	7.6	1.1	0.0	213	864	7.94	6.1	81
GL	L07219712	202.50	7.1	1.17	3.6	386	725	8.5	1.6	3.8	204	848	8.03	7.0	83
GL	L07219714	202.58	5.9	1.25	3.2	367	723	8.0	1.2	3.2	192	880	8.12	8.5	79
GL	L07219716	202.67							2.7	3.6	184	864	8.13	8.5	79
GL	L07279710	208.42							1.7	4.1	269	932	8.10	4.7	93
GL	L07279712a	208.50	7.7	1.17	3.8	463	793	8.2	1.5	4.1	274	916	8.02	6.9	95
GL	L07279712b	208.51	7.7	1.36	3.8	457	790	10.2	1.5	4.1	272	920	8.10	6.9	95
GL	L07279714	208.58	7.6	0.92	3.8	445	849	10.0	1.4	3.8	258	920	8.08	8.8	89
GL	L07279716	208.67	7.2	1.47	3.8	427	787	7.7	1.4	3.4	241	880	8.10	9.5	87
GL	L072997	210.00	47.8	1.49	5.3	406	776	1.5	25.7	0.0	301		0.26		
GL	L081197	223.00	89.0	2.06	59.8	405	741	6.0	15.7	7.1	231				
GL	L08119709	223.38							1.3	3.8	255	872	8.01	5.6	114
GL	L08119711	223.46	7.1	1.00	3.5	422	752	9.1	1.5	3.6	254	836	8.05	7.9	117
GL	L08119713	223.54	6.4	1.03	3.4	400	746	8.8	1.4	3.1	230	852	7.98	8.6	113
GL	L08119715	223.63	5.6	1.00	3.2	363	765	6.5	1.2	2.9	198	880	8.16	9.9	100
GL	L08179709	229.38	7.0	0.45	3.6	415	734	1.6	1.5	3.3	222	928	8.11	5.1	110
GL	L08179711	229.46	6.9	0.65	3.5	415	731	1.3	1.9	3.5	265	912	8.02	6.5	112
GL	L08179713	229.54	6.8	0.69	3.6	413	732	1.6	1.8	3.6	263	904	8.01	7.3	114
GL	L08179715	229.63	54.1	4.31	5.6	409	771	1.0	3.4	2.5	257	912	7.98	8.4	109
GL	L10039712	276.50	10.9	0.00	5.1	623	876	0.7	1.8	4.4	290	1092	7.35	3.1	146
GL	L10039716a	276.67	10.9	0.00	5.2	618	870	1.5	1.5	3.6	234	1076	7.69	3.1	140
GL	L10039716b	276.68	11.5	1.13	5.3	628	887	1.8	3.0	5.0	337	1064	7.60	3.1	139
GL	L111597	319.00	20.1	0.00	7.4	1198	1457	2.8	7.9	5.3	729	1824	8.07		249

Appendix 4 continued

Site	Sample Name	Day	Na$^+$ (μeq/l)	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	HCO$_3^-$ μeq/l (Titrated)	pH	T°C (of pH)	EC (μS/cm)
BR	IN050898	128.54	30.3	0.0	9.4	934	1168	1.8	14.7	0.0	181	1500	8.01	4.0	165
BR	IN051498	134.50	26.2	11.8	8.3	932	1207	2.0	9.0	0.0	190	1760	8.03	5.4	163
BR	IN051898	138.48	32.9	0.6	9.2	1042	1339	2.4	15.4	0.0	235	1780	8.10	5.9	198
BR	IN052198	141.54	30.0	0.0	8.7	1028	1297	1.9	10.7	0.0	244	1732	8.19	5.1	149
BR	IN052698	146.73	23.3	0.0	7.5	884	1137	2.3	8.1	1.1	223	1516	8.16	5.5	162
BR	IN052998	149.67	26.6	0.0	8.3	928	1163	2.4	8.7	0.0	276	1588	8.24	10.1	181
BR	IN060298	153.76	32.5	0.0	8.5	1019	1285	1.9	13.9	0.0	271	1912	8.28	8.0	193
BR	IN060498	155.67	34.6	0.0	7.7	1034	1291	2.4	13.9	0.0	251	2224	8.35	4.7	221
BR	IN061298	163.76	27.3	0.0	8.7	961	1186	2.9	7.0	1.2	268	1752	8.16	11.1	165
BR	IN061398	164.43	28.3	0.0	7.7	1014	1226	3.2	7.3	1.7	277	2160	8.23	5.1	162
BR	IN061798	168.67	33.9	0.3	7.8	1064	1310	2.5	10.1	0.0	273	1808	8.23	9.5	192
BR	IN062098	171.42	32.2	0.0	8.4	1092	1326	2.5	8.5	0.0	262	1672	8.14	5.8	203
BR	IN062598	176.60	28.7	0.0	8.1	1003	1234	2.6	6.7	0.0	287	1696	8.08	9.9	195
BR	IN062998	180.63	28.7	0.2	7.7	994	1227	2.2	7.3	2.4	287	1592	8.11	8.3	196
BR	IN063098	181.71	26.5	0.2	7.7	938	1170	2.3	6.0	0.0	276	1560	8.20	12.1	177
BR	IN070598	186.68	29.6	0.5	7.8	1047	1269	2.2	6.5	0.0	319	1632	8.15	7.9	205
BR	IN070698	187.59	28.3	0.0	7.4	1000	1229	2.2	6.2	1.1	302	1616	8.24	10.4	204
BR	IN071098	191.30	28.3	0.0	7.5	1039	1269	3.0	5.5	1.4	310	2304	8.15	6.0	202
BR	IN071398	194.46	31.4	0.0	7.8	1090	1328	2.6	6.2	1.4	310	1608	8.15	7.4	189
BR	IN072098	201.43	30.2	0.0	7.4	1071	1324	2.7	6.7	0.0	303	2700	8.01	6.7	183
BR	IN072298	203.52	27.3	0.3	7.4	1011	1280	2.3	5.4	1.1	305	1780	7.95	10.9	186
BR	IN072798	208.55	22.6	0.8	7.2	896	1229	2.3	6.1	2.2	276	1460	8.26	13.8	166
BR	IN073098	211.63	21.3	0.0	7.2	888	1266	2.6	4.1	0.0	264	1500	8.27	14.5	156

Appendix 5 1998 Stream Sample Chemistry. All concentrations in μeq/L. For sample name, first two letters designates the site, numbers give the sample date, and suffixes (e.g.A and B) designate duplicate samples. Day is the day of the year, fractions indicate specific hour of sampling when multiple samples were collected in one day.

Site	Sample Name	Day	Na$^+$ (μeq/l)	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	HCO$_3^-$ μeq/l (Titrated)	pH	T°C (of pH)	EC (μS/cm)
BR	IN080298	214.55	23.2	0.4	7.2	883	1205	2.6	5.1	2.0	284	1600	8.21	13.3	165
BR	IN080698	218.64	22.6	0.0	7.2	901	1224	2.4	5.7	1.4	303	1460	8.32	15.2	170
BR	IN080998	221.67	20.6	0.0	8.0	818	1153	1.8	3.9	1.2	293	1300	8.04	15.8	164
BR	IN081198	223.73	21.9	0.0	7.7	879	1190	2.1	4.0	2.2	343	1420	8.28	12.0	183
BR	IN081998	231.71	30.0	0.0	9.5	1178	1414	3.4	6.0	2.1	508	2280	8.41	13.1	205
BR	IN082098A	232.56	27.8	1.0	8.7	1144	1370	3.5	5.4	2.7	492	1640	8.28	13.9	207
BR	IN082198	233.67	28.8	0.4	8.8	1169	1385	3.4	5.7	0.0	507	1860	8.17	8.9	207
BR	IN082498	236.76	27.6	0.2	8.7	1127	1367	3.5	5.3	2.3	510	1480	8.03	10.6	190
BR	IN100298	275.58	37.8	4.8	10.0	1430	1642	3.0	8.2	3.1	658	1964	7.89	3.6	
GL	LG050898	128.64	10.6	0.0	5.5	742	1079	10.8				1136	8.10	3.9	149
GL	LG051298	132.46	13.7	9.7	7.6	712	1038	10.7	3.0	7.7	311	1200	7.98	2.9	144
GL	LG051298	132.54	10.7	0.0	5.3	726	1068	11.8	2.9	7.9	314	1184	8.02	4.1	142
GL	LG051298	132.63	10.5	0.4	5.5	724	1073	11.1	3.0	7.6	297	1160	8.07	4.8	148
GL	LG051298	132.71	9.7	13.5	5.0	649	980	9.2	7.7	7.9	294	1140	8.24	4.3	128
GL	LG051598	135.63	11.6	0.0	5.2	670	1022	12.0	2.6	7.7	350	1136	8.00	2.4	133
GL	LG052298	142.50	11.4	2.1	5.7	718	1040	12.9	10.2	8.3	353	1160	8.19	3.8	137
GL	LG052498	144.54	10.0	0.0	5.1	636	976	11.2	2.2	7.7	292	1104	8.08	5.9	143
GL	LG052698A	146.55	8.8	0.4	4.5	566	891	9.3	1.9	7.1	252	1104	7.92	4.1	139
GL	LG052698B	146.55	8.7	0.0	4.5	569	896	9.2	2.0	7.5	255	1088	8.03	4.1	138
GL	LG053098	150.46	9.2	0.3	4.0	522	862	11.3	1.8	7.1	292	1056	7.90	4.9	191
GL	LG060298A	153.56	12.4	0.0	5.1	653	1012	11.6	4.6	5.1	365	1224	8.07	6.3	259
GL	LG060498	155.56	11.1	0.0	4.6	647	988	11.4				1344	8.16	3.2	133
GL	LG061398	164.55	9.9	1.4	4.3	537	896	10.9	2.3	4.7	310	1056	8.14	5.3	114
GL	LG061798	168.56	10.5	4.2	4.6	635	983	12.4	2.4	6.4	358	1152	7.94	6.3	159
GL	LG062098	171.56	8.3	0.9	3.8	474	738	9.3				1032	8.31	7.3	144

Appendix 5 continued

Site	Sample Name	Day	Na^+ (µeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- µeq/l (Titrated)	pH	T°C (of pH)	EC (µS/cm)
GL	LG062498	175.48	21.2	33.7	6.3	609	993	11.6	3.2	5.8	307	1064	8.08	5.6	152
GL	LG062798B	178.50	10.4	0.0	4.5	558	930	11.4	2.3	6.0	328	952	7.92	5.6	130
GL	LG070298	183.59	9.7	1.1	4.2	604	986	9.4	3.8	6.0	338	1120	8.16	7.7	89
GL	LG070598	186.60	8.5	0.3	3.7	428	782	9.6	1.7	4.2	233	872	8.22	6.1	122
GL	LG070798	188.56	7.3	0.4	3.3	376	765	8.3	1.4	4.7	221	1144	8.15	8.6	109
GL	LG071198	192.59	8.0	0.5	9.1	395	774	8.9	9.4	4.1	226	760	8.24	7.2	121
GL	LG071598	196.43	9.5	0.0	4.0	535	902	9.4	2.8	4.3	313	1072	8.14	6.5	122
GL	LG071898	199.48	7.6	0.0	3.3	390	791	9.5	1.2	3.5	227	712	7.97	6.6	97
GL	LG072398	204.47	7.2	0.0	3.4	368	785	7.9	1.3	3.0	194		8.21	8.2	93
GL	LG072898	209.42	6.6	3.7	3.0	415	879	7.4	1.2	1.2	214	920	8.11	7.0	88
GL	LG072898	209.50	6.1	1.2	3.3	352	865	7.0	1.3	2.4	175	720	8.12	7.7	87
GL	LG072898	209.63	7.1	0.5	4.2	427	1065	6.0	1.5	1.4	166	700	8.29	10.1	87
GL	LG072898	209.71	6.4	1.4	3.9	378	942	6.5	1.6	1.8	153	780	8.36	9.3	85
GL	LG073198	211.51	6.4	0.3	3.0	337	750	7.5	1.3	2.8	212	780	8.22	7.0	91
GL	LG080598	217.58	8.2	0.5	4.3	289	824	5.1	3.3	2.4	169	660	8.51	11.6	100
GL	LG080898	220.52	7.1	0.0	3.4	371	862	8.3	1.5	3.6	207	700	7.88	9.4	98
GL	LG081298	224.64	5.5	0.0	2.7	279	779	6.1	1.3	1.9	152		8.25	7.7	94
GL	LG081498	226.64	5.8	0.5	2.9	281	820	5.6	1.6	3.2	172	480	8.43	9.0	86
GL	LG081998	231.63	9.5	0.3	4.2	480	871	9.5	2.8	3.1	352		8.15	10.5	121
GL	LG082198	233.54	12.1	0.0	6.6	486	909	10.4	5.2	0.0	335	740	7.62	6.9	108
GL	LG082498	236.67	6.8	0.2	3.2	358	774	7.3	2.1	2.8	259	880	7.84	7.9	94
GL	LG100398	276.67	11.6	9.9	4.5	617	998	11.9	3.9	3.2	484	924	7.82	4.1	120

Appendix 5 continued

Site	Sample	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	Temp °C	EC μS/cm
BR	IN050299	122.43	123.0	3.6	10.1	1543	1814	0.4	231.1	5.8	511	1940			284
BR	IN051199	131.63	121.2	1.1	9.6	1511	1800	2.7	160.8	5.0	490	2000	8.07		264
BR	IN051399	133.64	117.1	1.4	10.2	1538	1833	0.8	136.2	4.5	470	2432	8.22	6.1	242
BR	IN051999	139.46	93.7	1.2	9.5	1503	1824	2.3	99.9	5.0	444	2060	8.16	2.7	262
BR	IN052699	146.46	33.0	1.0	8.3	925	1123	0.0	19.2	0.0	203	1240	7.96	2.1	162
BR	IN053199	151.50	40.3	1.9	8.7	1121	1380	0.7	20.3	3.4	249	1240	8.03	2.5	182
BR	IN060299	153.52	41.0	1.2	8.1	1082	1358	0.0	21.4	0.0	232	2144	8.17	4.2	188
BR	IN060699	157.76	32.2	1.3	7.8	1004	1290	2.2	12.5	2.6	185	1720	8.25	4.5	
BR	IN061199	162.58	36.9	1.0	8.4	1098	1402	2.7	12.8	2.5	218	1833	8.24	8.2	196
BR	IN061499	165.38	28.6	1.1	7.3	978	1235	2.0	8.8	3.1	194	1753	8.07	3.2	165
BR	IN061699	167.63	19.6	0.9	7.2	768	1032	0.6	5.0	3.1	169	1487	8.17	8.8	145
BR	IN061699	167.48	21.2	1.9	7.2	835	1103	0.0	5.6	4.0	175	1487	8.05	7.1	153
BR	IN061699	167.75	20.6	0.9	7.3	802	1072	0.0	4.8	3.2	162	1413	8.07	7.3	142
BR	IN061699A	167.38	21.4	1.1	7.2	849	1104	1.6	5.8	4.9	173	1480	8.07	3.4	149
BR	IN061699B	167.38	22.0	0.9	7.8	857	1117	1.9	5.7	5.2	169	1500	8.15	3.4	149
BR	IN061999	170.46	23.2	1.4	7.8	867	1119	1.6	5.9	2.6	209	1540	8.09	5.6	158
BR	IN062299	173.55	28.4	0.7	7.8	950	1203	1.5	7.9	2.7	231	1987	8.09	5.8	147
BR	IN062699	177.56	31.7	0.9	7.5	1016	1284	1.9	8.3	2.0	267	1767	8.53	6.7	189
BR	IN071699	197.47	31.6	3.4	7.6	1027	1231	0.1	5.9	2.7	325	3200	8.18		207
BR	IN072299	203.58	26.8	0.0	7.2	973	1143	2.1	16.5	3.8	386	1667			182
BR	IN073099	211.63							3.9	0.0	419	1933			163
BR	IN080299	214.52							4.7	0.7	404	1760	8.30	10.8	154
BR	IN081399	265.67	31.3	0.0	8.7	1100	1289	5.0	4.6	0.0	487	1888	8.23		166
BR	IN082099	232.63	30.2	0.0	9.2	1092	1305	4.8	3.9	1.1	501	1760	8.19		168
BR	IN101899	291.67	43.4	2.8	9.0	1437	1608	2.8	10.1	4.5	627	2172	8.15		260
GL	LG021699	37.00	29.2	0.4	8.1	1294	1651	23.0	10.8	7.6	1218				
GL	Lg050199	121.60	17.4	2.3	6.7	1140	1515	20.4	8.4	9.0	991	1006	8.12		238
GL	LG051299	132.55	18.6	1.3	7.2	1213	1575	22.7	7.8	8.7	1007	1300	8.18		222

Appendix 6 1999 Stream Sample Chemistry. All concentrations in μeq/L. For sample name, first two letters designates the site, numbers give the sample date, and suffixes (e.g.A and B) designate duplicate samples. Day is the day of the year, fractions indicate specific hour of sampling when multiple samples were collected in one day.

Site	Sample	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	Temp °C	EC μS/cm
GL	LG051499	134.46	17.9	1.0	7.1	1226	1577	21.3	7.4	8.7	1010	1660	8.25	3.5	216
GL	LG052099A	140.46	17.7	1.1	7.1	1250	1606	22.6	6.8	8.7	888	1560	8.17	3.6	225
GL	LG052099B	140.46	17.4	1.0	7.2	1248	1599	20.5	7.0	9.0	899	1624	8.17	3.6	228
GL	LG052799	147.42	14.2	0.4	5.7	1072	1459	11.5	7.4	10.4	664	1592	7.99	3.9	203
GL	LG052799	147.59	15.0	1.1	6.2	970	1454	11.9				1004	8.10	5.6	192
GL	LG052899	148.56	15.7	0.9	6.1	1191	1620	12.2	9.2	9.7	820		8.11	4.5	219
GL	LG053099A	150.48	14.7	0.9	6.0	1028	1341	14.7	4.8	9.0	558	996	8.09	4.2	195
GL	LG053099B	150.48	14.7	0.7	5.9	1030	1343	15.0	4.8	9.2	554	1004	8.12	4.2	198
GL	LG060199	152.58	13.8	1.3	6.3	1003	1290	15.0	4.7	8.8	522	1532	8.13	3.6	180
GL	LG0603991	154.38	15.4	0.8	6.8	1077	1382	14.1	6.1	9.0	625	1692	8.16	1.7	
GL	LG0603992	154.50	15.7	0.9	6.3	1108	1427	15.4	6.0	9.6	638	1668	8.18	3.9	
GL	LG0603993A	154.63	14.9	0.7	6.3	1060	1372	14.9	5.9	9.2	621	1624	8.18	6.2	
GL	LG0603993B	154.63	15.6	0.8	8.1	1059	1371	15.2	5.8	8.7	602	1592	8.25	6.2	
GL	LG0603994	154.75	13.8	0.9	5.8	999	1288	13.9	5.4	8.5	588	1628	8.15	5.1	
GL	LG060499	155.55	13.9	1.1	6.4	1025	1294	12.8	4.4	8.8	463	1473	8.13	5.6	
GL	LG060799	158.55	15.2	0.8	6.2	1102	1448	14.2	7.4	9.8	655	1680	8.21	3.6	
GL	LG061299	163.51	15.7	0.7	6.6	1103	1395	14.5	7.4	8.8	637	1700	8.31	5.8	209
GL	LG061599	166.52	12.4	1.1	5.7	907	1210	10.1	5.4	10.0	436	1473	8.09		172
GL	LG061899	169.67	16.3	1.3	8.0	1300	1769	10.1	8.7	8.6	481	2220	8.04		232
GL	LG061899	169.42	15.2	0.6	7.1	1234	1670	10.3	8.3	9.1	458	2080	8.09	3.8	223
GL	LG062099	171.54	10.0	0.5	4.6	641	959	9.6	2.8	6.4	306	1033	8.08	4.8	122
GL	LG062399	174.64	10.6	0.8	4.6	664	956	10.1	3.1	7.0	328	1200	7.91	4.8	135
GL	LG062799	178.60	29.8	5.5	13.0	765	1046	12.1	4.6	6.8	374	1313	8.11	6.4	153
GL	LG071599	196.60	15.2	1.1	5.4	863	1223	11.4	6.2	8.0	414	1673	8.15		163
GL	LG072299	203.68	31.7	15.7	9.7	891	1273	10.2	5.6	7.6	389	2333			182
GL	LG072999	210.44	12.1	0.0	4.6	715	1109	13.3	3.9	4.5	293	1667	8.18	5.7	148
GL	LG080299	214.46	11.5	0.0	4.4	620	977	14.9	3.0	5.2	333	1600	8.08	7.0	149
GL	LG081599	227.58	9.9	0.0	3.9	498	909	11.8	2.8	3.5	327	1240	7.91		177
GL	LG101899	291.54	19.6	3.1	6.7	1224	1522	20.9	7.8	8.3	934	1648	8.07		235

Appendix 6 continued

Site	Sample Name	Time	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	Temp °C	EC μS/cm
BR	IN031800	900	78	44.90	0.28	8.89	1525	1710	0.3	8.5	6.7	689	2168	8.17		291
BR	IN042300	930	114	75.94	3.86	9.97	1430	1642	2.2	72.4	8.0	571	1980	8.19		292
BR	IN050200		123	88.45	1.23	10.16	1487	1761	1.8	104.2	5.9	471	2410	8.03		314
BR	IN050800	1440	129	87.04	0.61	9.36	1481	1788	2.3	105.3	5.3	414	2480	7.88		277
BR	IN051800	1320	139	57.33	0.78	11.69	1186	1492	1.8	41.2	5.2	227	2150	7.92	3.7	232
BR	IN052300	855	144	41.51	0.62	8.84	1075	1369	1.5	21.4	4.9	180	2047	7.65	0.4	196
BR	IN052600	1045	147	48.54	1.03	9.87	1261	1629	4.2	18.7	4.7	224	2177	7.99	1.6	208
BR	IN052900	1205	150	42.35	0.86	8.61	1178	1489	1.6	19.4	4.1	220	2213	8.00	4.3	211
BR	IN053000A	900	151	46.51	0.72	8.14	1150	1453	0.0	24.9	4.1	205	2273	8.31	2.0	200
BR	IN053000B	900	151	46.21	0.81	8.25	1144	1445	0.0	25.0	4.1	205	2207	8.35	2.0	199
BR	IN053000	1200	151	44.91	0.52	8.42	1156	1465	2.0	24.9	3.9	214		8.31	3.1	201
BR	IN053000	1500	151	44.47	0.69	8.76	1154	1459	2.2	21.8	3.9	212	2293	8.30	4.9	199
BR	IN053000A	1800	151	44.55	0.61	8.39	1151	1454	2.1	21.6	3.8	213	2207	8.33	3.6	201
BR	IN053000B	1800	151	43.56	0.88	8.31	1163	1466	1.8	21.1	4.0	208	2227	8.39	3.6	200
BR	IN053000	2100	151	34.69	0.99	7.98	1090	1359	0.0	13.5	3.8	213	2187	8.17	1.6	199
BR	IN060200	1210	154	27.46	0.00	7.43	971	1206	0.0	8.8	4.8	184	2347	8.38	5.1	181
BR	IN060500	1000	157	25.48	0.47	7.75	884	1144	0.0	6.9	3.9	161	1800	8.03	3.3	179
BR	IN061100	1300	163	27.87	1.10	7.88	948	1233	0.2	7.5	2.8	170	1817	7.89	5.5	178
BR	IN061300	900	165	27.98	0.77	7.61	953	1217	0.0	7.9	3.3	177	1867	8.28	2.9	173
BR	IN061300	1200	165	28.28	0.42	7.50	953	1231	0.0	7.5	2.8	177	1853	8.22	7.2	178
BR	IN061300A	1500	165	27.99	1.17	7.71	949	1239	1.8	7.1	2.8	171	1813	8.07	6.9	176
BR	IN061300B	1500	165	27.91	1.14	8.15	942	1236	1.7	7.7	2.7	171	1787	7.95	6.9	177
BR	IN061300	1800	165	27.72	0.84	7.77	942	1230	0.2	7.4	2.7	171	1787	8.15	6.1	164
BR	IN061300	2000	165	28.77	0.99	7.81	983	1281	1.6	7.3	2.4	193	1927	8.25	5.0	171
BR	IN061600	1423	168	27.03	0.75	7.26	979	1270	1.7	6.3	3.3	194	2033	8.24	10.0	176
BR	IN061900	1120	171	24.66	0.00	6.85	929	1186	0.0	5.4	3.5	199	1820	8.32	6.2	173
BR	IN062200	1112	174	29.48	0.59	7.44	998	1289	1.4	6.7	2.4	213	1793	8.02	4.3	175
BR	IN062500	1300	177	26.65	0.78	7.17	960	1230	0.0	5.3	3.1	217	1880	8.28	8.7	188
BR	IN062700	1210	179	25.40	0.00	7.45	947	1134	1.9	4.3	2.4	315	1733	8.26	7.3	182
BR	IN071900	1205	201	23.02	0.00	7.36	908	1074	2.3	3.8	2.6	336	1600	8.23	9.6	179
BR	IN072200	1220	204	25.02	0.00	7.25	935	1120	2.1	5.4	2.3	338		8.24	9.8	165

Appendix 7 2000 Stream and snow melt sample chemistry. All concentrations in μeq/L. For sample name, first two letters designates the site, numbers give the sample date, and suffixes (e.g.A and B) designate duplicate samples. Day is the day of the year.

Site	Sample Name	Time	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	Temp °C	EC μS/cm
GL	LG031800	1300	78	20.55	1.10	7.30	1312	1681	24.8	9.7	7.1	1213	1624	8.07		255
GL	LG042200	1100	114	19.42	4.14	7.13	1213	1571	20.2	9.0	9.0	1108	1420	8.24		265
GL	LG050300	1100	124	19.74	0.92	7.50	1249	1614	21.2	8.5	8.0	1018	1770	8.06		263
GL	LG050800	1110	129	19.35	0.61	6.89	1214	1578	20.7	8.6	7.8	980	1650	7.93		279
GL	LG051800	930	139	14.53	0.40	6.56	1060	1363	14.8	4.5	11.8	479	1760	8.02	0.9	224
GL	LG052300		144	16.07	0.40	6.84	1126	1422	15.0	5.2	9.8	554		8.01	2.1	198
GL	LG052600	1250	147	16.43	0.46	6.78	1124	1441	16.4	5.5	9.2	594	1847	8.14	3.0	198
GL	LG052900	1425	150	16.42	0.26	6.57	1139	1436	15.9	5.8	9.4	598	1723	8.46	5.6	193
GL	LG060100	900	153	16.96	0.33	6.91	1140	1436	15.9	6.1	9.3	597	1887	8.33	1.1	205
GL	LG060100A	1200	153	16.97	0.33	6.91	1142	1439	16.1	6.3	9.5	601	1760	8.33	4.0	199
GL	LG060100B	1200	153	16.87	0.45	6.83	1127	1425	15.8	6.0	9.5	592	1773	8.36	4.0	195
GL	LG060100A	1500	153	16.39	0.46	6.10	1081	1373	15.5	6.0	9.4	592	1827	8.43	6.0	193
GL	LG060100B	1500	153	15.58	0.59	6.50	1063	1348	15.6	5.5	9.1	563	1820	8.46	6.0	191
GL	LG060100	1800	153	15.32	0.85	6.41	1056	1333	15.7	5.3	9.4	543	1933	8.43	4.5	195
GL	LG060100	2100	153	15.98	0.81	6.93	1104	1385	14.8	6.7	9.7	565	1787	8.35	1.9	191
GL	LG060200	1320	154	14.12	0.64	6.13	1014	1277	11.8	4.3	11.0	433	1960	8.46	5.3	193
GL	LG060500	1505	157	14.98	1.56	8.36	890	1185	12.3	4.3	10.0	422	1687	7.93	3.5	183
GL	LG061100	1655	163	17.72	0.00	6.79	1099	1448	16.8	8.7	9.9	571	1560	8.29	3.2	169
GL	LG061500	900	167	14.16	0.00	5.79	936	1204	13.4	5.3	9.3	448	1700	8.20	1.9	202
GL	LG061500	1200	167	15.09	0.70	6.15	989	1277	12.4	7.1	9.3	509	1547	8.23	3.6	177
GL	LG061500A	1500	167	14.86	0.74	5.96	990	1278	13.2	6.7	9.1	510	1600	8.15	4.6	191
GL	LG061500B	1500	167	14.59	0.52	6.01	956	1232	12.7	5.4	9.2	467	1547	8.05	4.6	192
GL	LG061500	1800	167	14.75	0.64	6.15	968	1246	13.3	5.6	9.1	467	1580	8.31	3.4	184
GL	LG061500	2100	167	17.01	0.61	6.54	1093	1410	13.3	10.0	9.8	622	1620	8.27	2.4	174
GL	LG061600	1610	168	13.74	0.40	5.86	908	1165	12.7	4.1	9.2	401	1787	8.19	4.6	197
GL	LG061900	1350	171	12.91	0.50	5.64	832	1080	11.9	3.4	8.5	356	1487	8.33	4.3	155
GL	LG062200	1310	174	16.99	0.44	6.59	1126	1480	12.9	10.3	9.0	644	1447	8.25	3.3	161
GL	LG062500	1530	177	13.88	0.51	5.77	911	1211	11.5	7.3	7.7	444	1787	8.29	7.3	219
GL	LG062700	1425	179	14.42	0.00	5.27	980	1368	9.5	7.5	7.1	429	1597	8.27	7.0	182
GL	LG071900	1615	201	8.76	0.00	3.75	468	822	10.2	1.7	5.8	262	1700	8.25	7.6	197
GL	LG072200	1430	204	8.78	0.00	4.02	475	836	9.8	1.7	6.1	264	940	8.25	7.0	111

Appendix 7 continued

Site	Sample Name	Time	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	Temp °C	EC μS/cm
GL	LG072500	900	207	8.82	0.00	3.66	479	838	10.7	1.7	6.4	271	927		4.6	93
GL	LG072500	1200	207	9.35	0.00	3.53	470	829	10.3	1.9	6.3	272	933	8.24	6.8	109
GL	LG072500	1500	207	8.74	0.00	3.67	464	822	9.9	2.0	6.3	263	893	8.52	7.0	106
GL	LG072500	1700	207	11.62	0.00	5.00	770	1150	9.4	4.9	6.4	331	933	8.29	5.8	103
GL	LG072500	2100	207	45.12	0.00	11.93	1477	1968	0.0	15.7	15.0	516	1440	8.15	4.6	150

Site	Snow melt	Time	Day	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^- μeq/l (Titrated)	pH	Temp °C	EC μS/cm
Meadow	IN042200	1000	113	5.51	11.89	8.58	21	55	0.0	5.4	11.6	15	70	7.45		9
Meadow	IN050200		123	11.49	4.52	1.90	22	80	0.3	8.8	23.9	14	84	6.49		11
Meadow	IN050800	1500	129	6.52	4.27	0.68	17	43	0.0	4.2	11.7	6	51	6.22		6
Meadow	IN051700		138	4.13	3.23	0.55	16	32	0.1	2.2	6.4	3	70	6.04		4
Meadow	IN052400		145	2.32	2.78	0.29	9	16	0.0	0.7	3.2	2	37	6.29		2
Meadow	IN052900		150	2.06	2.43	0.25	7	12	0.1	0.4	2.6	2	36	6.11		2
Meadow	IN053100	1415	152	1.64	3.26	0.32	10	13	0.0	0.4	2.3	2	46	6.13		2
Forest	LG050800	1210	129	2.93	3.94	1.10	18	41	0.0	2.1	11.5	6	45	6.56		6
Forest	LG051700	1500	138	1.64	1.19	0.84	19	42	0.0	0.7	9.0	4	52	6.18		5
Forest	LG052400		145							2.2	3.8	3	318	7.36		29
Forest	LG052900		150	2.23	1.55	0.72	14	23	0.0	0.3	3.1	2	40	6.33		3
Forest	LG060200	1310	154	1.65	1.05	0.52	21	34	0.0	0.3	2.0	2	50	7.20		5

Appendix 7 continued

Site	Date (M/D/Y)	Layer	Top	Depth to Bottom	Thickness (cm)	Temp (C)	Density (g/ml)	SWE (cm)	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	pH	EC μS/cm
Forest	11/15/97	surface	<5cm						0.0	1.8	1.2	-2.2	-0.6	0.0	0.6	0.4	1.4	5.83	1.8
Meadow	11/15/97	surface	<5cm						0.7	1.7	1.5	-1.2	0.3	0.0	0.4	0.5	1.7	5.81	1.9
Outflow	11/15/97	surface	<5cm						0.1	1.2	0.1	0.1	9.1	0.0	0.1	0.8	1.2	6.01	1.8
Outflow	2/18/97	Layer A	0.0	6.0	6.0	-6.0	0.14	0.81	6.0	36.3	1.1	2.0	4.4	0.0	0.27	3.8	2.6	5.72	4.6
Outflow	2/18/97	Layer B	6.0	11.0	5.0	-4.0	0.25	1.25	1.5	0.6	0.2	0.0	0.9	0.0	0.35	2.8	1.6	5.51	5.5
Outflow	2/18/97	Layer C1	11.0	25.0	14.0	-5.0	0.29	4.06	7.2	2.4	0.9	6.3	8.1	0.0	0.43	1.4	1.0	6.28	2.5
Outflow	2/18/97	Layer C2	25.0	44.0	19.0	-0.9	0.32	5.99	7.4	2.7	1.1	3.1	26.6	0.0	0.72	1.3	2.0	6.35	3.1
Outflow	2/18/97	Layer D	44.0	60.0	16.0	-0.4	0.29	4.64	7.8	3.8	9.4	6.7	44.4	0.0	0.17	0.9	1.1	6.10	1.8
Outflow	2/18/97	Layer E	60.0	80.0	20.0	1.0	0.32	6.46	4.6	21.0	3.5	1.8	7.7	0.0	0.86	0.4	1.7	6.10	2.9
Outflow	3/25/98	Layer A	0.0	6.6	6.6	0.5	0.13	0.86	6.2	6.0	3.1	2.5	17.4	0.0	1.1	2.5	4.6	5.91	7.4
Outflow	3/25/98	Layer Ice	6.6	7.7	1.1		0.21	0.23	11.6	6.1	4.5	0.0	5.6	0.0	1.18	1.8	5.1	5.59	4.8
Outflow	3/25/98	Layer C	7.7	14.3	6.6	1.1	0.10	0.66	7.4	3.4	1.7	0.0	0.0	0.0	0.46	1.9	1.7	5.78	3.2
Outflow	3/25/98	Layer Ice	14.3	15.4	1.1		0.27	0.30	3.7	3.8	2.3	1.8	14,5	0.0	0.76	4.5	4.9	5.27	6.8
Outflow	3/25/98	Layer E	15.4	22.0	6.6	-0.4	0.23	1.52	2.5	5.7	0.4	11.1	14.1	0.0	0.37	1.7	2.9	5.72	3.9
Outflow	3/25/98	Layer F	22.0	41.8	19.8	0.2	0.29	5.74	5.6	3.4	0.3	0.5	2.3	0.0	0.28	3.9	3.1	5.48	5.5
Outflow	3/25/98	Layer G	41.8	61.6	19.8	0.6	0.31	6.14							0.3	2.0	1.1	5.76	3.4
Outflow	3/25/98	Layer H	61.6	70.4	8.8	0.3	0.26	2.29	9.0	2.7	4.2	0.0	17.8	0.0	1.08	1.4	2.1	6.17	6.9
Outflow	3/25/98	Layer I	70.4	88.0	17.6		0.18	3.17	5.4	34.4	1.7	0.9	10.6	0.0	0.51	1.7	2.0	6.21	2.3
Meadow	2/18/97	Layer A	0.0	6.0	6.0	-7.9	0.13	0.75	7.5	4.3	1.1	7.0	15.9	0.0	0.44	3.9	2.8	6.74	3.9
Meadow	2/18/97	Layer B	6.0	21.0	15.0	-7.4	0.24	3.60	6.3	2.1	0.7	-1.5	-0.4	0.0	0.22	2.4	1.3	5.81	3.1
Meadow	2/18/97	Layer C	21.0	32.0	11.0	-6.5	0.28	3.08	5.5	1.8	0.7	-13.5	-3.3	0.1	0.17	0.9	0.6	5.97	1.9
Meadow	2/18/97	Layer D	32.0	44.0*	12.0	-3.1	0.29	3.48							1.06	0.5	2.7	6.46	6.0

*(Depth to Vegetation)

Appendix 8 1997-1998 Snow Sample Chemistry and snow pit descriptions. All concentrations in μeq/L.

Site	Snow pit	Layer	Top	Depth to Bottom	Thick-ness (cm)	Temp (C)	Density (g/ml)	SWE (cm)	Na^+ (μeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	pH	EC uS/cm
Outflow	OF121598	A	0.0	7.0	7.0	-8.0	0.21	1.47	1.8	0.9	1.5	1.0	2.5	0.0	0.5	2.0	0.7	5.74	2.0
Outflow	OF121598	B	7.0	18.0	11.0	-4.0	0.14	1.54	2.1	4.4	0.3	0.4	1.2	0.0	0.3	2.2	1.2	5.78	1.6
Outflow	OF121598	C	18.0	40.0	22.0	-2.3	0.28	6.16	2.3	2.1	0.6	1.9	4.5	0.0	0.6	5.9	1.9	5.84	2.3
Outflow	OF121598	D	44.0	78.0	34.0	-1.8	0.32	10.88	3.0	4.2	0.5	1.0	2.7	0.0	1.3	2.8	1.0	5.99	1.7
Outflow	OF021699	A	0.0	12.0	12.0	-8.5	0.14	1.68	2.9	1.6	0.4	1.4	2.5	0.0	1.7	7.1	2.7	5.68	3.0
Outflow	OF021699	B	12.0	31.0	19.0	-11.1	0.25	4.75	1.7	2.8	0.2	1.5	4.1	0.0	0.9	8.1	2.9	5.69	2.9
Outflow	OF021699	C	31.0	44.0	13.0	-7.3	0.28	3.64	1.0	0.0	0.2	1.1	2.4	0.0	0.5	3.1	1.1	5.78	2.0
Outflow	OF021699	D	44.0	64.0	20.0	-5.7	0.30	6.00	6.1	2.9	0.7	12.6	50.9	0.0	0.6	2.3	1.0	5.88	1.7
Outflow	OF021699	E	78.0	89.0	11.0	-4.1	0.31	3.41	3.9	1.4	1.1	2.5	6.3	0.0	2.1	3.7	1.8	6.12	2.3
Outflow	OF021699	F	89.0	95.0	6.0	-3.3	0.29	1.74	1.9	0.0	0.3	1.0	2.0	0.0	0.3	1.8	0.6	6.06	1.5
Meadow	IN121598	A (1)	0.0	20.0	20.0	-8.3	0.07	1.40	1.6	1.1	0.3	0.0	0.0	0.0	0.5	1.2	0.5	5.82	1.6
Meadow	IN121598	A (2)	25.0	44.0	19.0	-4.6	0.15	2.85	3.0	2.0	0.3	4.8	13.8	0.0	1.5	7.0	4.0	6.14	4.7
Meadow	IN121598	B (1)	44.0	70.0	26.0	-3.4	0.23	5.98	2.9	2.7	0.2	3.3	5.5	0.0	0.8	4.3	1.6	5.84	2.2
Meadow	IN121598	B (2)	70.0	90.0	20.0	-3.4	0.27	5.40	2.1	2.5	0.4	1.6	4.3	0.0	0.9	1.5	1.7	5.96	1.8
Meadow	IN121598	B (3)	90.0	110.0	20.0	-1.6	0.31	6.20	0.0	2.4	0.2	0.3	5.1	0.0	0.5	2.0	1.1	5.94	1.7
Meadow	IN021599	A	0.0	11.0	11.0	-11.1	0.18	1.98	2.1	1.6	0.7	1.9	3.8	0.0	1.5	5.7	2.6	6.12	2.3
Meadow	IN021599	B	26.0	53.0	27.0		0.24	6.48	3.0	1.6	1.1	1.1	3.2	0.0	1.7	2.6	1.7	5.76	2.0
Meadow	IN021599	C	64.0	72.0	8.0		0.32	2.56	0.0	0.0	0.0	0.6	1.2	0.0	0.3	2.4	1.3	6.11	1.5
Meadow	IN021599	D (1)	83.0	96.0	13.0		0.38	4.94	1.0	0.5	0.2	1.6	3.5	0.0	0.2	2.6	0.8	5.95	1.8
Meadow	IN021599	D (2)	96.0	136.0	40.0	-1.0	0.26	10.40	1.1	1.2	0.1	1.6	4.0	0.0	0.2	2.5	0.9	5.93	1.6
Meadow	IN043099	A	0.0	7.0	7.0		0.44	3.08	2.5	3.2	0.4	11.7	14.7	0.0	0.9	1.5	0.7	6.47	2.8
Meadow	IN043099	Ice I3	7.0	8.0	1.0		0.60	0.60	4.1	4.5	0.9	2.4	4.1	0.0	1.6	1.1	2.0		
Meadow	IN043099	B	8.0	26.0	18.0	0.7	0.45	8.10	5.5	3.1	2.0	2.9	7.7	0.0	3.1	3.9	1.9	6.05	2.5
Meadow	IN043099	Ice I2	26.0	27.0	1.0		0.60	0.60	1.1	4.6	0.1	1.2	2.9	0.0	0.5	2.9	1.5	5.98	1.7
Meadow	IN043099	C	27.0	40.0	13.0	0.7	0.48	6.24	3.4	2.4	2.0	3.2	7.2	0.0	2.0	2.2	1.0	6.16	2.1
Meadow	IN043099	D (1)	40.5	65.0	24.5	0.4	0.47	11.52	1.9	4.6	0.2	2.8	6.2	0.0	0.4	3.2	0.9	6.10	1.8
Meadow	IN043099	D (2)	65.0	85.0	20.0	1.5	0.48	9.60	1.4	11.8	0.2	1.0	2.4	0.0	0.3	2.0	1.0	6.05	1.4
Meadow	IN043099	D (3)	85.0	100.0	15.0	1.2	0.46	6.90	3.5	2.8	1.0	0.7	2.6	0.0	1.4	2.1	0.7	6.00	1.8
Meadow	IN051299	A (1)	0.0	5.0	5.0	0.0	0.38	1.90	0.4	3.2	0.3	5.2	7.8	0.0	0.4	1.7	1.0	6.34	2.3
Meadow	IN051299	A (2)	5.0	11.0	6.0	0.0	0.44	2.64	0.9	2.3	0.5	0.0	0.0	0.0	1.7	1.6	0.7	5.74	1.5
Meadow	IN051299	B	11.0	26.0	15.0	0.2	0.41	6.15	1.0	6.4	0.4	0.6	1.4	0.0	0.5	1.4	0.8	5.69	1.4
Meadow	IN051299	C	26.0	56.0	30.0	0.3	0.40	12.00	1.9	2.7	0.6	0.0	2.1	0.0	0.7	1.4	0.6	6.14	1.3
Meadow	IN051299	D	56.0	72.0	16.0	0.5	0.30	4.80	2.1	4.3	16.7	27.8	28.1	0.0	1.0	0.0	1.6	6.00	6.3

Appendix 9 1999 Snow Sample Chemistry and snow pit descriptions. All concentrations in μeq/L.

Site	Snow pit		Top	Depth to Bottom	Thick-ness (cm)	Temp (C)	Density (g/ml)	SWE (cm)	Na⁺ (µeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	pH	EC uS/cm
Meadow	IN051999	A	0.0	12.0	12.0	0.4	0.40	4.80	0.7	4.0	0.2	2.1	0.9	0.0	0.5	1.0	0.5	6.51	1.8
Meadow	IN051999	B	12.0	21.0	9.0	0.1	0.43	3.87	2.3	103.8	1.1	3.6	-0.5	0.0	1.1	1.1	0.7	5.87	1.4
Meadow	IN051999	C1	21.0	48.0	27.0	1.3	0.41	11.07	1.1	2.5	0.5	-1.9	-3.3	0.0	0.6	1.7	0.7	5.84	1.3
Meadow	IN051999	C2	48.0	68.0	20.0	0.0	0.42	8.40	0.8	8.5	0.4	0.0	0.0	0.0	1.0	1.6	0.9	5.80	1.4
Meadow	IN052699	A	0.0	4.0	4.0	2.1	0.42	1.68	1.7	1.0	0.5	13.5	17.3	0.0	0.5	0.4	0.0	6.55	3.0
Meadow	IN052699	B	4.0	8.0	4.0	0.2	0.45	1.80	0.4	1.6	0.6	0.0	0.0	0.0	0.6	0.8	0.4	5.90	1.4
Meadow	IN052699	C1	8.0	34.0	26.0	0.5	0.35	9.10	0.0	2.9	2.4	2.5	0.3	0.0	0.3	0.0	0.5	5.74	2.0
Forest	LG021699	A	0.0	8.0	8.0	-9.0	0.12	0.96	2.7	1.7	0.8	4.2	11.0	0.0	1.9	6.4	3.7	5.82	1.6
Forest	LG021699	B	8.0	28.0	20.0	-9.5	0.22	4.40	3.2	2.8	2.5	3.8	13.4	0.0	3.3	6.1	4.7	6.14	4.7
Forest	LG021699	C	28.0	57.0	29.0	-5.7	0.31	8.99	2.0	2.9	0.8	4.1	11.9	0.0	0.4	3.4	2.5	5.84	2.2
Forest	LG021699	D	57.0	89.0	32.0	-4.4	0.28	8.96	2.1	1.8	1.1	1.6	4.4	0.0	0.7	1.6	1.2	5.96	1.8
Forest	LG021699	E	89.0	104.0	15.0	-2.7	0.24	3.60	1.9	2.1	1.0	2.4	5.7	0.0	1.7	2.1	1.0		
Forest	LG050199	A	0.0	8.0	8.0	1.8	0.39	3.12	3.0	3.9	1.3	5.1	10.3	0.0	2.2	1.5	1.0	6.40	2.5
Forest	LG050199	B	9.0	20.0	11.0	0.7	0.41	4.51	6.0	12.0	2.8	4.4	10.2	0.0	1.9	3.2	2.7	6.18	2.6
Forest	LG050199	C	20.0	28.0	8.0	0.7	0.44	3.52	2.4	9.7	0.7	4.3	8.7	0.1	0.7	4.3	2.9	6.16	2.5
Forest	LG050199	Ice I2	28.0	29.0	1.0		0.63	0.63	2.8	2.3	0.7	6.2	9.5	0.0	1.3	2.1	2.2	6.32	2.1
Forest	LG050199	D	29.0	56.0	27.0	0.4	0.38	10.26	4.0	24.2	3.0	7.4	16.4	0.0	2.5	2.0	1.3	6.12	3.7
Forest	LG050199	E1	56.0	75.0	19.0	1.5	0.37	7.03	3.4	2.6	1.7	3.1	7.8	0.0	9.1	2.3	1.4	5.98	2.1
Forest	LG051299	A	0.0	3.0	3.0	0.3	0.29	0.87	1.0	3.2	0.6	10.0	17.5	0.0	0.5	1.2	0.7	6.34	3.2
Forest	LG051299	B	3.5	9.0	5.5		0.39	2.15	2.2	26.3	0.9	3.1	4.3	0.0				6.00	1.9
Forest	LG051299	C	9.0	21.0	12.0	0.6	0.41	4.92	1.9	4.2	1.2	2.1	5.0	0.0	1.6	2.9	2.1	5.83	2.3
Forest	LG051299	Ice I2	21.0	23.0	2.0		0.60	1.20	1.4	5.4	0.9	4.8	5.3	0.0				6.30	2.1
Forest	LG051299	D	23.0	44.0	21.0	0.7	0.42	8.82	9.2	20.3	5.3	19.4	55.4	0.0	0.8	1.4	1.4	6.21	1.8
Forest	LG051299	E1	44.0	65.0	21.0	0.1	0.37	7.77	1.4	0.8	1.5	5.6	9.6	0.0	1.3	1.5	1.4	6.13	2.5
Forest	LG051299	E2	65.0	89.0	24.0	0.2	0.36	8.64	6.9	18.6	7.8	8.5	15.6	0.0	2.9	2.0	8.5	6.27	4.6
Forest	LG052099	A	2.0	11.0	9.0	0.6	0.39	3.51	0.4	2.0	0.3	2.4	3.2	0.0	0.5	0.0	0.9	6.57	1.8
Forest	LG052099	Ice	11.0	15.0	4.0		0.60	2.40	2.5	0.0	1.0	2.7	7.3		1.1	1.5	0.6	7.08	1.5
Forest	LG052099	B	15.0	36.0	21.0	1.0	0.38	7.98	0.2	1.5	0.6	1.1	2.6	0.0	0.6	1.0	1.2	6.19	1.7
Forest	LG052099	C	36.0	60.0	24.0	0.6	0.30	7.20	0.7	2.3	1.9	0.8	0.6	0.0	0.9	0.0	0.8	5.99	1.9
Forest	LG052099	D	60.0	72.0	12.0	0.2	0.30	3.60	1.1	16.0	5.4	10.6	15.7	0.0	2.8	0.0	1.7	6.22	4.6
Forest	LG052799	A	0.0	4.0	4.0		0.41	1.64	1.8	40.8	1.7	16.5	25.2	0.0	0.8	0.4	0.4	6.69	4.1
Forest	LG052799	B	4.0	11.0	7.0	0.4	0.47	3.29	1.9	0.9	0.4	8.3	12.4	0.0	0.6	1.4	0.9	6.32	1.7
Forest	LG052799	C1	11.0	35.0	24.0	0.2	0.39	9.36	2.2	23.6	2.0	6.1	9.0	0.0	1.5	1.1	0.6	6.29	2.5
Forest	LG052799	C2	35.0	47.0	12.0	1.0	0.37	4.44	2.2	9.9	2.0	6.3	9.3	0.0				6.44	2.2

Appendix 9 continued

Site	Date	Layer	Day	Top (cm)	Bottom (cm)	Thick-ness (cm)	Temp (C)	Density (g/ml)	SWE (cm)	Na$^+$ (μeq/l)	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	pH	EC uS/cm
Meadow	01/29/00	A	29	83.8	68.6	15.2	-14.9	0.20	3.0	4.7	2.1	0.22	3.0	8.3	0.0	3.3	7.3	2.6	5.7	2.4
Meadow	01/29/00	B	29	68.6	63.5	5.1	-10.1	0.22	1.1	4.7	1.6	0.48	5.1	22.0	0.0	3.5	8.7	4.2	6.3	3.2
Meadow	01/29/00	C	29	63.5	53.3	10.2	-5.6	0.21	2.1	3.8	2.3	1.42	2.7	7.9	0.0	3.5	6.3	2.3	5.7	3.7
Meadow	01/29/00	D	29	53.3	30.5	22.9	-4.3	0.21	4.8	8.3	1.8	0.45	2.6	16.5	0.0	1.2	4.6	2.1	6.3	2.3
Meadow	01/29/00	E	29	30.5	25.4	5.1	-2.8	0.26	1.3											
Meadow	01/29/00	F	29	25.4	0.0	25.4	-1.3	0.22	5.6	6.0	2.6	2.22	1.9	5.7	0.0	3.8	2.4	2.0	5.9	2.1
Meadow	03/18/00	A	78	120.0	102.0	18.0	-2.9	0.18	3.2	4.0	2.2	1.65	5.1	14.3	0.0	3.3	12.3	4.1	5.4	4.7
Meadow	03/18/00	B	78	102.0	90.0	12.0	-2.6	0.19	2.3	1.9	1.3	1.98	2.5	7.7	0.0	2.4	5.9	1.6	6.2	1.7
Meadow	03/18/00	C	78	90.0	68.0	22.0	-1.5	0.22	4.8	2.7	0.5	2.07	5.8	30.9	0.2	3.6	6.6	2.5	6.0	3.34
Meadow	03/18/00	D	78	68.0	49.0	19.0	-1.4	0.21	4.0	2.4	1.0	0.91	3.6	8.9	0.0	1.5	3.9	1.6	6.3	1.65
Meadow	03/18/00	E	78	49.0	14.0	35.0	-0.5	0.24	8.4	3.1	2.4	1.84	3.4	9.8	0.0	1.7	3.0	1.8	6.4	1.81
Meadow	03/18/00	F	78	14.0	0.0	14.0	-0.3	0.29	4.1	2.3	7.9	4.14	5.5	7.9	0.0	1.8	1.7	1.4	5.5	1.85
Meadow	04/21/00	A	112	84.0	80.0	4.0		0.36	1.4	2.3	1.4	0.40	9.6	26.7	0.0	0.9	2.6	1.3	6.6	3.3
Meadow	04/21/00	B	112	80.0	75.0	5.0		0.34	1.7	2.6	4.7	0.37	4.6	11.3	0.0	1.4	5.9	5.3	6.2	2.6
Meadow	04/21/00	C	112	75.0	65.0	10.0		0.24	2.4	4.5	1.4	0.28	4.6	11.0	0.0	2.5	6.4	1.7	6.1	2.1
Meadow	04/21/00	D	112	65.0	45.0	20.0		0.22	4.4	2.3	1.4	0.24	3.4	11.7	0.0	0.4	5.6	2.3	6.0	1.9
Meadow	04/21/00	E	112	45.0	30.0	15.0		0.27	4.1	11.1	1.9	0.47	4.0	13.1	0.0	1.2	5.0	3.2	6.4	2.5
Meadow	04/21/00	F	112	30.0	0.0	30.0		0.29	8.7	2.5	2.3	0.25	2.2	5.8	0.0	0.3	2.5	2.4	5.9	1.3
Meadow	05/02/00	A	123	72.0	64.0	8.0	1.3	0.38	3.0	2.9	1.4	0.18	15.0	22.5	0.0	0.8	3.1	1.0	6.6	3.4
Meadow	05/02/00	B	123	64.0	52.0	12.0	0.9	0.41	4.9	2.9	1.4	0.18	4.7	8.1	0.0	1.1	3.0	0.9	6.2	1.5
Meadow	05/02/00	C	123	52.0	28.0	24.0	0.8	0.39	9.4	2.7	1.5	0.24	3.5	8.1	0.0	0.4	3.2	1.2	6.1	1.5
Meadow	05/02/00	D	123	28.0	0.0	28.0	0.5	0.31	8.7	2.4	1.7	0.26	3.0	5.4	0.0	0.3	1.7	1.2	6.0	1.4
Meadow	05/09/00	A	130	55.0	34.0	21.0	0.4	0.43	9.0	1.7	1.6	0.20	5.8	10.6	0.0	0.7	1.5	0.6	6.5	2
Meadow	05/09/00	B	130	34.0	23.0	11.0	0.6	0.4	4.4	3.0	2.1	0.25	6.1	10.4	0.0	0.6	2.2	0.8	6.3	1.8
Meadow	05/09/00	C	130	23.0	0	23.0	0.5	0.34	7.8	2.7	1.7	0.48	2.4	5.8	0.0	0.6	1.3	1.4	6.1	1.2
Meadow	05/17/00	A	138	38.0	25.0	13.0	-1.9	0.46	6.0	1.1	0.9	0.23	11.2	15.0	0.0	0.5	0.9	0.4	5.9	2.43
Meadow	05/17/00	B	138	25.0	14.0	11.0	-2.5	0.45	5.0	1.6	0.5	0.12	7.0	10.0	0.0	0.4	1.3	0.7	5.9	1.84
Meadow	05/17/00	C	138	14.0	0	14.0	-1.3	0.51	7.1	2.3	1.9	0.72	5.0	6.9	0.0	1.1	0.8	0.6	5.6	1.86
Meadow	05/24/00	A1	145	25	0	25		na		1.5	2.4	0.43	5.2	9.4	0.0	0.4	1.4	0.9	5.9	1.44
Meadow	05/24/00	A2	145	25	0	25		na								0.4	1.4	0.9	5.9	1.44
Forest	01/29/00	A	29	85.1	73.7	11.4	-16.0	0.20	2.3	3.2	2.3	0.4	3.7	8.3	0.00	1.7	8.4	2.6	5.7	2.3
Forest	01/29/00	B	29	73.7	63.5	10.2	-11.5	0.42	4.3	2.8	1.2	0.6	4.1	18.2	0.00	1.1	6.4	3.0	6.2	2.3
Forest	01/29/00	C	29	63.5	53.3	10.2	-9.8	0.20	2.0	1.8	1.1	0.4	1.6	5.0	0.00	0.4	3.9	1.6	5.7	1.6
Forest	01/29/00	D	29	53.3	48.3	5.1	-5.6	0.33	1.7	4.2	1.3	0.2	4.3	12.9	0.00	0.4	6.3	3.2	6.0	1.9
Forest	01/29/00	E	29	48.3	43.2	5.1	-3.1	0.23	1.2	6.7	3.6	0.6	5.2	15.9	0.00	0.9	9.3	4.1	6.1	3.0
Forest	01/29/00	F	29	43.2	22.9	20.3	0.1	0.23	4.7											

Appendix 10 2000 Snow Sample Chemistry and snow pit descriptions. All concentrations in μeq/L.

Site	Date	Layer	Day	Top (cm)	Bottom (cm)	Thick-ness (cm)	Temp (C)	Density (g/ml)	SWE (cm)	Na^+ (µeq/l)	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	pH	EC uS/cm
Forest	01/29/00	G	29	22.9	0.0	22.9		0.29	6.6	1.6	1.1	0.5	2.8	6.1	0.00	0.2	3.0	1.7	5.9	1.4
Forest	03/18/00	A	78	94.0	89.0	5.0	-2.3	0.31	1.6	4.9	0.5	11.8	6.9	16.4	0.00	7.6	11.3	4.9	6.6	4.1
Forest	03/18/00	B	78	89.0	72.0	17.0	-1.9	0.20	3.4	4.7	2.7	0.8	1.7	4.6	0.00	1.7	11.6	5.0	5.0	4.4
Forest		ICE1	78	72.0	68.0	4.0	-1.0	0.29	1.2											
Forest	03/18/00	C	78	68.0	58.0	10.0	-0.5	0.25	2.5	2.1	1.0	0.6	2.2	5.5	0.00	0.5	5.0	1.1	6.0	2.3
Forest		D	78	58.0	45.0	13.0	-0.2	0.27	3.5										6.6	2.9
Forest	03/18/00	E	78	45.0	31.0	14.0	0.8	0.24	3.4	3.7	0.9	0.7	3.4	9.9	0.00				6.4	2.1
Forest		ICE2	78	31.0	27.0	4.0		0.34	1.4											
Forest	03/18/00	F	78	27.0	0.0	27.0		0.36	9.7	2.9	1.3	0.4	3.0	9.3	0.00	0.8	3.0	2.4	5.9	2.3
Forest	04/22/00	A	113	106.0	94.0	12.0	1.2	0.36	4.3	2.4	3.5	0.6	2.6	6.6	0.00	0.5	3.8	2.3	5.9	1.7
Forest	04/22/00	B	113	94.0	78.0	16.0	1.0	0.45	7.2	2.7	3.0	0.4	3.2	8.3	0.00	0.8	12.2	6.1	5.2	4.7
Forest	04/22/00	C	113	78.0	55.0	23.0	1.1	0.35	8.1	2.7	1.4	0.4	10.9	40.5	0.00	0.6	8.0	5.4	6.3	
Forest	04/22/00	D	113	55.0	45.0	10.0	1.1	0.42	4.2	2.8	1.6	0.4	11.1	42.5	0.00	0.6	8.0	5.4	6.7	4.7
Forest	04/22/00	E	113	45.0	0.0	45.0	1.0	0.30	13.5	3.8	4.2	1.9	4.2	10.3	0.00	0.8	4.3	2.7	6.0	2.1
Forest	05/03/00	F	124	95.0	90.0	5.0	1.4	0.53	2.7	2.0	2.5	0.4	5.6	10.6	0.00	1.7	1.4	0.8	6.4	2.7
Forest	05/03/00	E	124	90.0	70.0	20.0	1.4	0.47	9.4										6.0	1.9
Forest	05/03/00	D	124	70.0	63.0	7.0	0.7	0.39	2.7	3.3	3.5	0.7	4.9	10.5	0.00	1.5	2.8	1.2	6.2	1.7
Forest	05/03/00	C	124	63.0	58.0	5.0	1.9	0.49	2.5	3.7	3.3	0.7	7.7	13.5	0.00	1.9	2.9	1.2	6.4	2.4
Forest	05/03/00	B	124	58.0	50.0	8.0	2.6	0.43	3.4	3.7	3.2	0.6	8.9	23.1	0.00	1.5	5.1	1.9	6.5	3.5
Forest	05/03/00	A	124	50.0	0.0	50.0	1.7	0.30	15.0	7.6	3.3	1.3	6.8	16.1	0.00	1.8	5.4	3.2	6.2	3.2
Forest	05/08/00	A	129	83.0	78.0	5.0	2.7	0.31	1.6	1.7	3.0	0.4	8.5	16.0	0.00	0.3	3.4	1.8	6.3	2.5
Forest	05/08/00	B	129	78.0	58.0	20.0	3.1	0.42	8.4	1.8	1.7	0.2	2.2	4.9	0.00	0.2	2.7	0.8	5.9	1.4
Forest	06/08/00	C	129	58.0	34.0	24.0	2.6	0.31	7.4	1.9	1.3	0.2	4.7	13.2	0.00	0.3	4.4	2.0	6.2	1.9
Forest	05/08/00	D	129	34.0	0.0	34.0	1.9	0.30	10.2	1.7	2.3	0.3	2.7	6.6	0.00	0.3	1.7	1.5	6.0	1.4
Forest	05/17/00	A	138	81.0	68.0	13.0	3.4	0.46	6.0	2.4	1.9	0.4	4.9	10.9	0.00	0.6	1.4	0.5	6.1	1.9
Forest	05/17/00	B	138	68.0	57.0	11.0	2.9	0.60	6.6	2.1	0.3	0.3	9.4	36.1	0.00	0.4	4.9	1.9	6.3	4.0
Forest	05/17/00	C	138	57.0	42.0	15.0	1.9	0.30	4.5	2.0	1.7	0.3	3.5	9.0	0.00	0.4	3.8	2.0	5.4	1.9
Forest	05/17/00	D	138	42.0	0.0	42.0	2.4	0.31	13.0	1.9	2.1	1.5	3.9	10.3	0.16	2.5	2.2	1.9	5.6	1.8
Forest	05/24/00	A	145	45	30	15.0		0.4	6.0	1.5	0.9	0.3	4.6	12.6	0.05	0.9	2.0	1.4	5.9	1.8
Forest	05/24/00	B	145	30	15	15.0		0.38	5.7	2.5	1.9	0.3	3.5	8.7	0.00	0.4	2.6	1.6	5.7	1.5
Forest	05/24/00	C	145	15	0	15.0		0.41	6.2	1.4	1.7	0.3	2.6	6.9	0.00	0.3	1.9	1.4	5.8	1.2

Appendix 10 continued.

Site	1998 Samples	DOC (ppm)	Site	1998 Samples	DOC (ppm)	Site	1999 Samples	DOC (ppm)
BH	BH051198	1.09	BG	UG051198	0.48	GL	LG051899	0.19
BH	BH052098	0.42	BG	UG051598	0.95	GL	LG052099	0.27
BH	BH053098	0.43	BG	UG052098	0.26	GL	LG052799	0.43
BH	BH060398	0.43	BG	UG053098	0.45	GL	LG052899	0.39
BH	BH061598	0.62	BG	UG060398	0.39	GL	LG053099 A	0.38
BH	BH062598	0.49	BG	UG062598	0.24	GL	LG060199	0.36
BH	BH070298	0.56	BG	UG070298	0.35	GL	LG060399 9:00	0.39
BH	BH081298	0.29	BG	UG071898	0.31	GL	LG060399 12:00	0.38
BH	BH081998	0.48	BG	UG072998 A	0.45	GL	LG060399 15A	0.40
BR	IN050898	1.63	BG	UG080398	0.50	GL	LG060399 18:00	0.39
BR	IN051498	1.37	BG	UG081298	0.30	GL	LG060499	0.37
BR	IN052198	1.13	BG	UG081998	0.43	GL	LG060799	0.35
BR	IN052998	0.98	**Site**	**1999 Samples**		GL	LG061299	0.35
BR	IN060498	1.02	BH	BH052199	0.38	GL	LG061599	0.28
BR	IN061398	0.92	BH	BH052899	0.45	GL	LG061899 10:00	0.69
BR	in062598	0.74	BH	BH060199	0.40	GL	LG061899 16:00	0.77
BR	IN070698	2.53	BH	BH060499	0.44	GL	LG062099	0.21
BR	IN072098	0.55	BH	BH060799	0.43	GL	LG062399	0.21
BR	IN080698	0.70	BH	BH061299A	0.38	GL	LG062799	0.22
BR	IN081198	0.50	BH	BH061599	0.32	GL	LG080299	0.39
BR	IN082098 A	0.51	BH	BH061899	0.45	GL	LG081599	0.42
GL	LG050898	0.50	BH	BH062099	0.26	GL	LG082199	0.15
GL	LG050898	0.43	BH	BH062399A	0.27	NT	NTJ061499	0.30
GL	LG052298	0.33	BH	BH062799	0.27	NT	NTJ062699	0.38
GL	LG053098	0.42	BR	IN050299	0.92	OF	OF051399	0.49
GL	LG060498	0.62	BR	IN051199 15:15	0.90	OF	OF051999	0.66
GL	LG061398	0.71	BR	IN051399	1.01	OF	OF052899	2.23
GL	LG062498	0.32	BR	IN051999	0.94	OF	OF053199	1.41
GL	LG070298	0.34	BR	IN052699	1.95	OF	OF060299	1.30
GL	LG070798	0.35	BR	IN053199	1.60	OF	OF060699	1.90
GL	LG071898	0.32	BR	IN060299	1.66	OF	OF061199	1.00
GL	LG081998	0.45	BR	IN060699	1.80	OF	OF061499	1.12
OF	OF050898	1.59	BR	IN061199	1.35	OF	OF061699	1.35
OF	OF051298	1.02	BR	IN061499	1.39	OF	OF061999	1.14
OF	OF051498	1.41	BR	IN061699 12:00	1.47	OF	OF062299	0.93
OF	OF052198	1.12	BR	IN061699 15:00	1.57	OF	OF062699	0.80
OF	OF052998	1.41	BR	IN061699 18:00	1.59	OF	OF081199	0.70
OF	OF061498	2.31	BR	IN061699 9:00A	1.43	OF	OF082099	0.45
OF	OF062598	0.89	BR	IN061999	1.43	BG	UG052199	0.26
OF	OF070698	0.81	BR	IN062299	1.25	BG	UG052899	0.52
OF	OF070698	0.63	BR	IN062699	1.17	BG	UG060199	0.20
OF	OF071398	0.73	BR	IN071399	0.71	BG	UG060499	0.22
OF	OF080298	0.56	BR	IN073099	0.46	BG	UG060799	0.16
OF	OF080698	0.58	BR	IN080299	0.51	BG	UG061399	0.18
OF	OF081198 B	0.59	BR	IN082099	0.36	BG	UG061599	0.19
OF	OF082098 11:00	0.45	GL	LG051299	0.26	BG	UG061899	0.14
			GL	LG051499	0.24	BG	UG062099	0.16
						BG	UG062399	0.34

Appendix 11 DOC concentrations for 1998 and 1999 stream samples. For sample name, first two letters designates the site, numbers give the sample date, and suffixes (e.g.A and B) designate duplicates and sample times.

Sample Name	DOC ppm	Sample Name	DOC ppm
IN031800 A	0.32	LG060100 1	0.48
IN042100	0.36	LG060100 1	0.54
IN042100	0.36	LG060100 1	0.41
IN042300	0.53	LG060100 2	0.41
IN050200	0.85	LG060100 9	0.56
IN050800	0.87	LG060200	0.46
IN050800	0.83	LG060500	0.46
IN051800	1.90	LG061100	0.41
IN052300	2.12	LG061500 1	0.39
IN052600	1.61	LG061500 1	0.40
IN052900	1.65	LG061500 1	0.39
IN053000 12:00	1.75	LG061500 1	0.39
IN053000 12:00	1.67	LG061500 2	0.39
IN053000 15:00	1.77	LG061600	0.48
IN053000 15:00	1.71	LG061900	0.33
IN053000 18:00A	1.59	LG062200	0.30
IN053000 18:00B	1.61	LG062500	0.43
IN053000 21:00	1.66	LG062700	0.43
IN053000 9:00A	1.73	LG071900	0.41
IN053000 9:00B	1.82	LG072200	0.18
IN060200	1.65	LG072500 1	0.17
IN060500	1.50	LG072500 1	0.23
IN061100	1.77	LG072500 2	0.33
IN061300 12:00	1.61	LG072500 9	0.20
IN061300 15:00A	1.70	NT050300	0.37
IN061300 15:00B	1.65	NT052300	0.46
IN061300 18:00	1.62	NT053000	0.45
IN061300 21:00	1.65	NT061300	0.42
IN061300 9:00	1.56	NT062200	0.40
IN061600	1.56	NT072600	0.56
IN061900	1.29	OF050800	0.41
IN062200	1.17	OF051900	0.91
IN062500	1.22	OF052300	0.68
IN062700	1.00	OF052600	0.87
IN071900	0.52	OF052600	0.81
IN072200	0.44	OF052900	0.82
IN072600	0.52	OF060200	2.03
LG031800 A	0.18	OF060500	1.82
LG031800 B	0.16	OF061100	2.04
LG042200	0.16	OF061300	0.85
LG050300	0.25	OF061600	1.64
LG050800	0.23	OF062200	0.81
LG051800	0.50	OF062500	0.91
LG052300	0.71	OF062700	0.85
LG052300	0.71	OF071900	0.51
LG052600	0.47	OF072200	0.52
LG052600	0.46	OF072600	0.55
LG052900	0.42		
LG060100 12:00a	0.46		
LG060100 12:00B	0.45		

Snow/Snow Melt	DOC (ppm)	Snow/Snow Melt	DOC (ppm)
INA012900	0.34	LGD050300	0.17
INB012900	0.31	LGE050300	2.17
INC012900	0.17	LGF050300	0.23
IND012900	0.35	LGA050800	0.44
INF012900	0.20	LGB050800	0.20
INA031800	0.32	LGC050800	0.25
INB031800	0.18	LGD050800	0.19
INC031800	0.19	LGA051700	0.51
IND031800	0.21	LGB051700	0.56
INE031800	0.42	LGC051700	0.65
INF031800	0.20	LGD051700	1.00
INA042100	0.16	IN042100 melt	1.38
INB042100	0.29	IN050200 melt	0.88
INC042100	0.22	IN050800 melt	0.46
IND042100	0.26	IN051700 melt	0.26
INE042100	0.26	IN052400 melt	0.22
INF042100	1.09	IN052900 melt	0.30
INA050200	0.15	IN053100 melt	0.48
INB050200	0.15	LG042200 melt	2.06
INC050200	0.14	LG050800 melt	0.75
IND050200	0.15	LG051700 melt	0.89
INA050900	0.17	LG052400 melt	4.69
INB050900	0.18	LG052900 melt	0.77
INC050900	0.19	LG060200 melt	1.06
INA051700	0.55		
INB051700	0.58		
INC051700	0.26		
LGA012900	0.21		
LGA012900	0.22		
LGB012900	0.40		
LGC012900	0.23		
LGC012900	0.23		
LGD012900	0.29		
LGE/F012900	0.28		
LGG012900	0.26		
LGA 031800	0.29		
LGA031800	0.31		
LGB031800	0.55		
LGC031800	0.20		
LGD031800	0.45		
LGE031800	0.56		
LGF031800	9.27		
LGA042200	0.30		
LGB042200	0.29		
LGC042200	0.23		
LGD042200	0.27		
LGE042200	0.32		
LGA050300	0.31		
LGB050300	0.19		
LGC050300	0.35		

Appendix 12 DOC concentrations for 2000 stream, snow and snowmelt samples. For sample name, first two letters designates the site, numbers give the sample date, and suffixes (e.g.A and B) designate duplicates and sample times. Site LG=GL(Glacial), IN=BR(Bow River), OF (outflow), NT (Numtijah well water)

Site	Sample Name	Dilution	DOC (ppm)
BR	IN053000 S1 24cm	5x	6.8
BR	IN060500 S1 24cm	5x	4.8
BR	IN061100 S1 24cm	5x	4.9
BR	IN061700 S1 24cm	5x	4.9
BR	IN062000 S1 24cm	5x	4.9
BR	IN062300 S1 24cm	5x	5.3
BR	IN062600 S1 24cm	5x	5.2
BR	IN062800 S1 24cm	5x	5.8
BR	IN072000 S1 24cm	5x	19.4
BR	IN072300 S1 24cm	5x	23.3
BR	IN072700 S1 24cm	5x	23.4
BR	IN060500 S1 12cm	10x	83.5
BR	IN061100 S1 12cm	5x	65.3
BR	IN062000 S1 12cm	10x	40.2
BR	IN062300 S1 12cm	10x	32.1
BR	IN062600 S1 12cm	10x	32.7
BR	IN072000 S1 12cm	5x	20.1
BR	IN072300 S1 12cm	10x	26.2
BR	IN072700 S1 12cm	5x	22.4
BR	IN060500 S2 24cm	5x	11.0
BR	IN061100 S2 24cm	5x	10.1
BR	IN062000 S2 24cm	5x	12.3
BR	IN062300 S2 24cm	5x	11.3
BR	IN062600 S2 24cm	5x	12.0
BR	IN062800 S2 24cm	5x	10.2
BR	IN072000 S2 24cm	10x	31.6
BR	IN072300 S2 24cm	10x	30.3
BR	IN072700 S2 24cm	10x	30.8
BR	IN060500 S2 12cm	5x	17.5
BR	IN061100 S2 12cm	5x	23.3
BR	IN062000 S2 12cm	5x	29.4
BR	IN062600 S2 12cm	10x	31.4
BR	IN062800 S2 12cm	10x	30.5
BR	IN072000 S2 12cm	10x	37.6
BR	IN072300 S2 12cm	5x	39.0
BR	IN072700 S2 12cm	10x	35.4
GL	LG060500 S1 12cm	5x	6.8
GL	LG061100 S1 12cm	5x	3.9
GL	LG061700 S1 12cm	5x	5.1
GL	LG062000 S1 12cm	5x	5.2
GL	LG062300 S1 12cm	5x	4.9
GL	LG062600 S1 12cm	5x	6.2
GL	LG062800 S1 12cm	5x	6.2
GL	LG072000 S1 12cm	5x	24.9
GL	LG072300 S1 12cm	5x	18.4
GL	LG072700 S1 12cm	10x	24.0
GL	LG061100 S1 24cm	5x	4.5
GL	LG061700 S1 24cm	5x	5.2
GL	LG062000 S1 24cm	5x	5.5
GL	LG062300 S1 24cm	5x	5.7
GL	LG062600 S1 24cm	5x	6.3
GL	LG062800 S1 24cm	5x	7.2
GL	LG072000 S1 24cm	5x	24.1
GL	LG072300 S1 24cm	5x	17.4
GL	LG072700 S1 24cm	10x	23.4
GL	LG062300 S2 12cm	5x	13.7
GL	LG062600 S2 12cm	5x	6.2
GL	LG062800 S2 12cm	5x	6.5
GL	LG072300 S2 12cm	10x	32.2
GL	LG072700 S2 12cm	10x	20.0
GL	LG062000 S2 24cm	5x	6.2
GL	LG062300 S2 24cm	5x	6.3
GL	LG062600 S2 24cm	5x	6.6
GL	LG062800 S2 24cm	5x	6.9
GL	LG072300 S2 24cm	5x	25.8
GL	LG072700 S2 24cm	10x	25.5

Appendix 13 DOC concentrations for 2000 soil water samples. For sample name, first two letters designates the catchment in which soils were sampled, numbers give the sample date, and suffixes (e.g.S1 and S2) designate soil site and depth of the soil lysimeter. The S1 sites were near the stream at similar elevations, S2 were at slightly higher elevations (one slopes or moraines). Dilution, is the dilution factor used to determine the DOC concentration. Concentrations are corrected for the DOC content of the water used to dilute the sample.

Site	Sample	Day	DOC (ppm)	FI	λFmax	Site	Sample	Day	DOC (ppm)	FI	λFmax
BR	IN031800	77	0.32	1.52	447	NT	NT050300	123	0.37	1.68	431
BR	IN042100	112	0.36	1.54	454	NT	NT052300	133	0.46	1.68	444
BR	IN050800	129	0.87	1.50	446	NT	NT053000	151	0.45	1.65	455
BR	IN051800	139	1.90	1.44	455	NT	NT061300	165	0.42	1.66	437
BR	IN052300	143	2.12	1.46	453	NT	NT062200	174	0.35	1.63	443
BR	IN053000_18	151.75	1.59	1.45	456	NT	NT072600	207	0.56	1.67	446
BR	IN060500	157	1.50	1.45	452	BR Soil	INS0611c	163	4.90	1.50	452
BR	IN0605ft	157	1.50	1.46	456	BR Soil	INS0617c	169	4.90	1.51	452
BR	IN061300	165.88	1.65	1.43	456	BR Soil	INS0620c	172	4.90	1.49	456
BR	IN062200	174	1.17	1.45	457	BR Soil	INS0623c	175	5.30	1.48	454
BR	IN071900	201	0.52	1.46	451	BR Soil	INS0626c	178	5.20	1.47	451
BR	IN072200	203	0.44	1.46	454	BR Soil	INS0628c	180	5.80	1.50	452
BR	IN072600	208	0.52	1.43	448	GL Soil	LGS0611C	163	4.50	1.47	453
GL	LG031800	77	0.18	1.60	434	GL Soil	LGS0617c	169	5.20	1.46	455
GL	LG050300	124	0.25	1.58	447	GL Soil	LGS0620c	172	5.50	1.46	453
GL	LG050800	129	0.23	1.72	429	GL Soil	LGS0623c	175	5.70	1.45	456
GL	LG051800	139	0.50	1.58	448	GL Soil	LGS0626c	178	6.30	1.45	454
GL	LG052300	143	0.71	1.58	446	GL Soil	LGS0720c	202	24.10	1.54	457
GL	LG060100_18	153.75	0.41	1.60	450	GL Soil	LGS0727c	209	23.40	1.55	452
GL	LG060500	157	0.46	1.56	450	Meadow melt	INM0502	123	0.88	1.58	440
GL	LG061500	167.88	0.33	1.54	447	Meadow melt	INM0508	129	0.46	2.06	415
GL	LG071900	201	0.41	1.49	452	Meadow melt	INM0517	138	0.26	1.43	418
GL	LG072200	203	0.18	1.72	423	Meadow melt	INM0524	145	0.22	1.78	425
GL	LG072500	207.71	0.23	1.62	410	Meadow melt	INM0529	150	0.30	1.60	433
OF	OF050800	128	0.41	1.65	442	Meadow melt	INM053100	152	0.48	1.80	453
OF	OF051900	140	0.91	1.47	454	Forest melt	LGM0422	112	2.06	1.49	446
OF	OF052300	144	0.68	1.57	450	Forest melt	LGM0508	129	0.75	1.33	460
OF	OF052900	150	0.82	1.48	452	Forest melt	LGM0517	138	0.89	1.35	456
OF	OF060200	153	2.03	1.40	455	Forest melt	lgm052900	149	0.77	1.35	461
OF	OF060500	157	1.82	1.53	451	Forest melt	LGM0602	154	1.06	1.87	448
OF	OF061100	163	2.04	1.60	446	Forest melt	LGM0524	145	4.69	1.34	456
OF	OF062200	174	0.81	1.45	447						
OF	OF071900	201	0.51	1.51	457						
OF	OF072200	203	0.52	1.66	442						
OF	OF072600	208	0.55	1.45	454						

Appendix 14 DOC and Fluorescence of DOC. FI= Fluorescence Index and λFmax = wavelength of maximum fluorescence.

Sample	Day	Time	$\delta^{18}O$	δD
BH051198	131	1430	-21.7	
BH053098	150	1345	-21.2	
BH062298	173	1530	-21.3	
BH070598	186	1215	-20.8	
BH072498	205	1050	-20.1	
BH072498	205	1650	-20.0	-145.5
BH081998	231	1250	-19.5	
BH100398	276		-19.9	
IN050898	128	1300	-21.5	
IN062598	176	1430	-21.2	
IN070598	186	1620	-21.1	
IN072798	208	1330	-20.7	-156.6
IN081198	223	1750	-20.6	-153.9
IN082098B	232	1340	-20.4	
IN100298	275		-20.5	
LG050898	128	1530	-21.3	
LG052498	144	1300	-21.2	
LG060498	155	1340	-20.8	
LG062498	175	1145	-20.9	
LG071198	192	1415	-20.5	
LG072898	209	1000	-20.3	-152.9
LG081998	231	1520	-19.9	-150.4
LG100398	276		-19.8	
OF050898	128	1025	-21.2	
OF062598	176	1600	-21.0	
OF070698	187	1140	-21.2	-158.6
OF082098	232	1100	-20.5	-154.6
OF100298	275		-20.3	
RS060298	153	1130	-13.5	-109.8
RS061998	170	1500	-17.7	-157.7
RS063098	181	1115	-18.7	-149.1
UG051198	131	1220	-20.8	
UG062298	173	1440	-21.0	
UG070598	186	1115	-20.9	
UG071298	193	1115	-20.9	-155.1
UG072498	205	1130	-20.6	
UG072498	205	1730	-20.6	-151.8
UG072998A	210	1340	-20.5	
UG072998B	210	1340	-20.6	
UG081998	231	1220	-20.5	-153.3
UG100398	276		-19.8	

Appendix 15 Oxygen ($\delta^{18}O$) and deuterium (δD) isotope ratios of 1998 water samples (streams, and rain). Isotopes were measured at the Environmental Isotope Laboratory (EIL), University of Waterloo. Sites: BH (Bow Hut), LG=GL (Glacial), IN=BR(Bow River), OF (outflow), NT (Numtijah well water), RS (Rain), UG=BG(Bow Glacier).

Stream Sample	Day	Time	$\delta^{18}O$	δD	Snow Sample	Day	Height (cm)	$\delta^{18}O$
BH052899	148	1100	-21.8	-167.7	IN041599_A	46	130.5	-25.2
BH060799	158	1010	-21.7		IN041599_B	46	96.5	-25.4
BH061299A	163	1400	-21.8		IN041599_C	46	68.0	-20.4
BH061599	166	1450	-22.7		IN041599_D	46	20.0	-24.3
BH061899	169	1230	-22.8	-174.2	IN043099_A	120	96.5	-21.9
BH062799	178	1100	-22.1		IN043099_I3	120	92.5	-22.6
IN051399	133	1530	-21.5	-164.8	IN043099_B	120	83.0	-23.7
IN053199	151	1200	-21.9		IN043099_I2	120	73.5	-23.5
IN060699	157	1830	-22.0	-167.1	IN043099_C	120	66.5	-24.1
IN061199	162	1400	-21.8		IN043099_D1	120	47.3	-26.2
IN061699	167	1145	-22.4		IN043099_D2	120	25.0	-21.1
IN061699	167	1500	-22.4		IN043099_D3	120	7.5	-23.6
IN061699	167	1800	-22.0	-170.7	IN051299_A1	132	69.5	-22.2
IN061699A	167	900	-22.4		IN051299_A2	132	64.0	-22.3
IN061999	170	1115	-22.2		IN051299_B	132	53.5	-25.1
IN062699	177	1335	-21.7		IN051299_C	132	31.0	-23.8
IN072299	203	1400	-22.8		IN051299_D	132	8.0	-25.6
IN073099	211	1500	-21.7		IN051999_A	139	62.0	-22.3
IN080299	214	1250	-22.3		IN051999_B	139	51.5	-23.8
IN081399	225	1600	-22.1	-170.8	IN051999_C1	139	33.5	-25.6
IN082099	232	1500	-22.0		IN051999_C2	139	10.0	-23.8
IN101899	291	1600	-21.5	-166.6	IN052699_A	146	32.0	-23.4
LG051299	132	1315	-20.6	-157.6	IN052699_B	146	28.0	-22.5
LG052099A	140	1115	-20.7		IN052699_C	146	13.0	-23.6
LG052799	147	1015	-21.4		LG041699_A	47	100.0	-24.8
LG052799	147	1415	-21.4		LG041699_B	47	86.0	-22.7
LG060399A	154	1500	-20.6	-159.5	LG041699_C	47	61.5	-25.7
LG060799	158	1330	-21.2		LG041699_D	47	31.0	-24.2
LG061299	163	1230	-21.0		LG050199_A	121	90.0	-21.4
LG061599	166	1240	-22.0		LG050199_B	121	79.5	-24.6
LG061899	169	1000	-21.3		LG050199_I2	121	70.0	-23.0
LG061899	169	1600	-21.1	-159.1	LG050199_C	121	65.5	-23.1
LG062099	171	1300	-21.3		LG050199_D	121	51.5	-26.4
LG062799	178	1430	-21.3		LG050199_E1	121	28.5	-24.5
LG071599	196	1445	-21.8	-164.9	LG051299_A	132	87.5	-21.0
LG072299	203	1630	-21.9		LG051299_I1	132	85.8	-22.3
LG072999	210	1045	-21.8		LG051299_B	132	82.8	-22.8
LG080299	214	1100	-21.7	-163.5	LG051299_C	132	74.0	-22.8
LG081599	227	1400	-21.0		LG051299_I2	132	67.0	-23.3
LG082099	232	1300	-21.6		LG051299_D	132	55.5	-24.6
LG101899	291	1300	-20.9	-161.2	LG051299_E1	132	34.5	-24.1
NTJ061499	165		-21.2	-160.0	LG051299_E2	132	12.0	-24.7
NTJ062699	177	1430	-21.3	-160.6	LG052099_A	140	65.5	-22.8
OF051399A	133	1145	-20.7	-158.9	LG052099_I	140	59.0	-23.1
OF053199	151	1400	-20.7		LG052099_B	140	46.5	-25.4
OF060699	158	1630	-21.2	-164.6	LG052099_C	140	24.0	-25.0
OF061199	162	1600	-20.5		LG0527099_A	147	45.0	-23.5

Appendix 16 Oxygen ($\delta^{18}O$) and deuterium (δD) isotope ratios of 1999 water samples (streams, rain, and snow). Isotopes were measured at EIL, University of Waterloo. Sites: BH (Bow Hut), LG=GL (Glacial), IN=BR(Bow River), OF (outflow), NT (Numtijah well), RS (Rain), UG=BG (Bow Glacier).

Stream Sample	Day	Time	$\delta^{18}O$	δD
OF061999	170	1620	-21.2	-162.4
OF062699	177	1100	-21.0	
OF071799	198	1015	-21.1	-160.8
OF072199	203	1500	-21.1	
OF073199	212	1145	-21.1	
OF081199	223	1615	-21.1	-160.1
OF101799	290	1100	-21.0	-159.6
R060299	153	1000	-17.5	-137.4
R060699	157	1630	-3.5	-83.1
R062699	177	1100	-18.4	-152.3
UG052899	148	1145	-20.7	-160.2
UG060799	158	1000	-20.8	
UG061299	163	1430	-20.9	
UG061599	166	1540	-21.4	
UG061899	169	1250	-20.5	-152.0
UG062099	171	1105	-20.6	
UG062799	178	1215	-20.2	

Snow Sample	Day	Height (cm)	$\delta^{18}O$
LG0527099_B	147	39.5	-23.0
LG0527099_C1	147	24.0	-22.7
LG0527099_C2	147	6.0	-23.0

Appendix 16 continued

Stream Sample	Day	Time	$\delta^{18}O$
IN042300	114	930	-20.8
IN050200	123		-20.8
IN050800	129	1440	-20.1
IN051800	139	1320	-21.1
IN052600	147	1045	-21.1
IN052900	150		-19.7
IN053000A	151	900	-20.5
IN053000	151	1500	-20.6
IN053000	151	2100	-20.7
IN060500	157	1000	-21.0
IN061100	163	1300	-20.9
IN061300	165	900	-21.1
IN061300	165	1200	-21.2
IN061300A	165	1500	-21.1
IN061300	165	2000	-20.9
IN062200	174	1112	-21.1
IN062700	179	1210	-21.0
LG042200	114	1100	-20.7
LG050300	124	1100	-20.0
LG050800	129	1110	-19.8
LG051800	139	930	-20.9
LG052600	147	1250	-20.6
LG060100	153	900	-20.7
LG060100A	153	1500	-20.3
LG060100	153	2100	-20.6
LG060200	154	1310	-19.9
LG060500	157	1505	-21.0
LG061100	163	1655	-20.7
LG061500	167	900	-21.2
LG061500	167	1200	-21.1
LG061500A	167	1500	-21.0
LG061500	167	2100	-21.1
LG062200	174	1310	-21.0
LG062700	179	1425	-21.1
LG072500	207	900	-20.7
LG072500	207	1200	-20.7
LG072500	207	1700	-20.8
LG072500	207	2100	-20.5
NT050300	124	1430	-20.2
NT052300	144	1200	-20.2
NT053000	151	1200	-20.3
NT061300	165	1620	-21.0
NT062200	174	1450	-20.6
NT072600	208	1300	-20.6
RAIN052900	150	1630	-12.4
RAIN061100	163	950	-13.4
RAIN061400	166	1200	-16.9
RAIN061800	170	2030	-13.0
RAIN072500	207	1900	-13.4

Soil Solutions	Day	Time	$\delta^{18}O$
IN060500S1_24	157	1015	-19.7
IN061100S1_24	163	1315	-19.4
IN062000S1_24	172	1110	-19.1
IN062600S1_24	178	1135	-18.9
IN060500S1_12	157	1026	-18.0
IN061100S1_12	163	1422	-18.2
IN062000S1_12	172	1150	-17.6
IN062600S1_12	178	1210	-17.1
IN060500S2_24	157	1226	-19.3
IN060500S2_12	157	1235	-19.2
IN062000S2_12	172	1223	-18.4
LG060500S1_12	157	1500	-18.8
LG061100S1_12	163	1730	-16.8
LG062000S1_12	172	1455	-16.8
LG061100S1_24	163	1755	-18.8
LG062000S1_24	172	1520	-19.0
LG062600S1_24	178	1530	-18.5
LG062600S2_12	178	1640	-18.4
LG062000S2_24	172	1610	-21.7
LG062600S2_24	178	1715	-20.5

Snow Pack	Day	Height (cm)	$\delta^{18}O$
IN01/29/00_A	29	76.2	-27.9
IN01/29/00_B	29	66.0	-27.1
IN01/29/00_C	29	58.4	-26.8
IN01/29/00_D	29	41.9	-24.5
IN01/29/00_F	29	12.7	-20.5
IN04/21/00_A	112	82.0	-20.4
IN04/21/00_B	112	77.5	-17.9
IN04/21/00_C	112	70.0	-25.7
IN04/21/00_D	112	55.0	-26.6
IN04/21/00_E	112	37.5	-24.1
IN04/21/00_F	112	15.0	-20.6
IN05/09/00_A	130	44.5	-21.4
IN05/09/00_B	130	28.5	-22.1
IN05/09/00_C	130	11.5	-20.5
IN05/24/00_A1	145	12.5	-20.4
IN05/24/00_A2	145	12.5	-20.4
LG01/29/00_A	29	74.3	-27.4
LG01/29/00_B	29	63.5	-25.6
LG01/29/00_C	29	55.9	-26.5
LG01/29/00_D	29	48.3	-25.8
LG01/29/00_E	29	35.6	-22.4
LG01/29/00_G	29	11.4	-20.5
LG04/22/00_A	113	92.0	-19.6
LG04/22/00_B	113	74.5	-24.9
LG04/22/00_C	113	61.5	-24.3
LG04/22/00_D	113	27.5	-25.8
LG04/22/00_E	113	22.5	-22.3
LG05/08/00_A	129	70.5	-17.0
LG05/08/00_B	129	56.0	-22.7
LG05/08/00_C	129	29.0	-24.7
LG05/08/00_D	129	17.0	-20.6
LG05/24/00_A	145	30.0	-24.0
LG05/24/00_B	145	15.0	-22.0
LG05/24/00_C	145	7.5	-20.9

Snow Melt	Day	Time	$\delta^{18}O$
IN042200	113	1000	-19.3
IN050200	123		-24.4
IN050800	129	1500	-23.9
IN051700	138		-23.4
IN052400	145		-20.4
IN052900	150		-19.7
IN053100	152	1415	-20.6
LG042100	112	1300	-15.6
LG050800	129	1210	-23.1
LG051700	138	1500	-23.5
LG052400	145		-22.2
LG052900	150		-19.6
LG060200	154	1310	-19.9

Appendix 17 Oxygen isotope ratios ($\delta^{18}O$) of water samples (streams, soil solutions, snows, and snow melt) from 2000. Isotopes were measured at EIL, University of Waterloo. Sites: LG=GL (Glacial), IN=BR(Bow River), OF (outflow), NT (Numtijah well), RS (Rain).